Coordination chemistry of the calix[6]arene system: application in polymerisation catalysis and beyond

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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Abstract: This perspective looks at structurally characterized examples of metal-based calix[6]arene complexes, focusing on the coordination chemistry adopted and their applications, primarily in polymerisation catalysis. In particular, we look at our attempts to utilize the ability of the calix[6]arene system to accommodate multiple metal centres, and where appropriate, we compare the catalytic behaviour with that of other metallocalix[*n*]arenes formed from commercially available calix[*n*]arenes, *i.e.* the smaller but more common calix[4]arene and the larger calix[8]arene system. We also discuss how synthetic efforts are now targeting calix[6]arenes for which a change of the bridge can provide additional possibilities, *i.e.* heteroatom bridged tetrahomodioxacalix[6]arenes (containing -CH₂OCH₂- bridges) and tetrahomo diazacalix[6]arenes (containing -CH₂N(R)CH₂- bridges, R typically is methyl). The outlook for the future, in terms of the use of calix[6]arene-based catalysts is also discussed.

Introduction

Interest in calix[n]arenes and the coordination chemistry thereof continues to grow and is driven by the broad uses for which they are now being utilized. These include a variety of medical applications,¹ their use in liquid crystals,² in the nuclear industry,³ and as sensors/extractants.⁴ When compared against other macrocycles, calix[*n*]arenes find significance because of the extensive organic derivatization that is possible at either rim. Specific calix[n]arenes have attracted attention, for example the interest and potential of the calix[8]arene system, particularly in relation to molecular magnets, has recently been highlighted.⁵ Benefits of this large calixarene include its varying degrees of deprotonation and conformational flexibility which allows for the facile formation of multi-metallic species. Moreover, the degree of metalation can be controlled, and mixed-metal systems are readily accessible. We previously highlighted the early coordination chemistry work on large calix[n]arenes (n \geq 6) in a comprehensive review back in 2003.⁶ Since that time, calixarene metal chemistry has flourished, although most of the work is still focused on the more common calix[4]arene system, which is known to prefer a cone conformation upon metalation and for which the majority of complexes are monometallic.⁷ The remaining calix[n] arene, other than n = 4 or 8, that is commercially available in significant quantities is the calix[6]arene system.8 In this perspective, we discuss the ability of the calix[6]arene system to allow for the isolation of novel structural motifs, and how the resulting metal species can be employed for the production of polymers, including traditional petroleum-based polyolefins as well as biodegradable polymers. After initially

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⁺ Dedicated to Professor Takehiko Yamato on the occasion of his 70th birthday.

discussing the parent calixarene, this perspective review covers the complexes by metal type with alkali metals considered first and then transition metals by group number and then looks at main group systems.

Lanthanide/actinide systems are mentioned but only in brief. More recent work that has made use of changing the methylene bridges, *i.e.* use of dimethyleneoxa (-CH₂OCH₂-) or aza (-CH₂N(Me)CH₂-) bridges is also highlighted (see Fig. 1). We note that a number of reviews have discussed the use of broader calixarene catalysts for polymer production,⁹ and wider catalysis.¹⁰ We also note that beyond polymerisation catalysis, the use of calix[6]arene, particularly titanocalix[6]arenes, is attracting interest in photocatalysis,¹¹ and we highlight recent work here too.

Throughout the review, given the complexity of some of the structures, we provide chem draw representations alongside the molecular structures where necessary to aid the reader. The full names of these compounds, as depicted in the CSD, are provided in the appendix.



Figure 1. Depiction of the parent calix[6]arene structures left: calix[6]areneH₆/*p*-*tert*-butylcalix[6]areneH₆; middle: *p*-*tert*-

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butyltetrahomodioxacalix[6]areneH₆; right methyldimethyldiazacalix[6]areneH₆.

The preparation of p-*tert*-butylcalix[6]areneH₆ (L⁶H₆, Fig. 1, left) was first reported by Gutsche *et al.*¹² and is now well established with yields of 90% readily achievable.^{13,14} The molecular structure of L⁶H₆ has been determined as a number of solvates, ¹⁵ and the influence of the solvent on the conformation has been noted.¹⁶ We have previously reported acetonitrile clathrates including the solvates with 1.5 (CCDC No. 215817) and 2 acetonitrile (CCDC No. 215818) molcules.¹⁷ In each of these solvates, the macrocycle adopts a pinched cone conformation, see Fig. 2.



Figure 2. Molecular structures of the acetonitrile solvates of L^6H_6 as reported in reference 17.

Group 1 metals

Back in 1990s, a number of calix[6]arene structures containing K⁺ ions were reported by Murayama and Aotei,¹⁸ and later K⁺, Rb⁺ and Cs⁺ complexes were reported by Hanna *et al*. ¹⁹ and by Zheng *et al*. ²⁰ These reports centred around the use of either KOH or M₂CO₃ (M = K, Rb, Cs) and their structures have been reviewed by us previously.⁶

As part of a study into the use of larger calixarenes as catalysts for the ring opening polymerisation (ROP) of the cyclic esters ε caprolactone (ε -CL), δ -valerolactone (δ -VL) and *rac*-lactide (*r*-LA), our group reacted *p*-*tert*-butylcalix[6]areneH₆ (L⁶H₆) with LiOtBu in THF, which led to the isolation in 15% yield of the complex [Li₁₄(L⁶H)₂(CO₃)₂(THF)₆(OH₂)₆)·14THF (**1**·14THF).





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Figure 3. The structure of $[Li_{14}(L^6H)_2(CO_3)_2(THF)_6(OH_2)_6]\cdot 14THF (1\cdot 14THF).$

The core of the structure (CCDC No. 2084712, see Fig. 3), which is about 12 Å long, possesses a chain of five Li_2O_2 diamonds, which is sandwiched between monoprotonated L⁶H ligands. The bridging CO_3^{2-} groups are thought to arise via exposure to atmospheric CO₂. In the ⁷Li NMR spectrum, only five different types of lithium centres are observed. NMR studies at elevated temperatures revealed no changes suggesting the structures were stable under the conditions employed for the ROP.²¹

When screened for the ROP of ε -CL (with and without benzyl alcohol, BnOH, present), this Li₁₄ complex performed well with low catalysts loadings (1:1000) achieving 56% conversion over 8 h at 130 °C, whilst as a melt (ca. 80% conversion) highest molecular weights (M_n = 16.13 x 10^3 Da) and good control (D = 1.18, where D is the polydispersity index) were observed. Under the same conditions, this calix[6]arene complex outperformed a number of lithiated calix[8]arenes species, [Li₁₀(L⁸)(OH)₂(THF)₈]·7THF, namelv $[Li_{18}(deBuL^8)_2(OtBu)_2(THF)_{14}]$ ·4THF (deBuL⁸H₈ = calix[8]areneH₈) and $[Li_4(L^8H_4)(OH_2)_4(THF)_6]$ 5.5THF, with the superior activity attributed to the enhanced lability of the ligands present. The L⁴H₄ derived $[LH_2Li_2(THF)(OH_2)_2] \cdot 3THF]$ (L^4H_4) complex = p-tertbutylcalix[4]areneH₄)²² was also less active in the presence of one equivalent of BnOH.

The mechanism for the ROP here was thought to be the coordination insertion route (see Fig. 4) requiring an M-OR linkage, though the low molecular weights obtained (*versus* calculated values) suggested there was extensive transesterification taking place. For δ -VL ROP, kinetic studies revealed a similar trend in activity with transesterification evident. MALDI-ToF spectra of products revealed linear polymers with HO/OBn end groups and cyclic polymers had formed in a ratio of about 50:50. In the case of *r*-LA, ROP screening in the presence of one equivalent of benzyl alcohol again revealed that the calix[6]arene complex outperformed the calix[8]arene systems. MALDI-ToF spectra of the PLA revealed the presence of HO/OBn end groups.

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Figure 4. The coordination/insertion mechanism by a metal alkoxide (M-OR) species.

Group 2 metals

Strontium

Reaction of strontium metal with L⁶H₆ in isopropanol and subsequent addition of [Ti(OiPr)₄] led to the isolation of the {Ti(L⁶H₂)₂[Sr(OiPr)(H₂O)][Sr(OiPr)₂}·7iPrOH·0.5CH₂Cl₂·H₂O (**2**·7iPrOH·0.5CH₂Cl₂·H₂O) in 75% yield. In the structure (CCDC 221944, Fig. 5), each six-coordinate strontium centre was bound by four oxygens of an L⁶H₂ ligand plus either an isopropanol ligand and a water molecule or two isopropanol ligands; there were no π -arene interactions present.²³





Figure 5. Structure of 2·7*i*PrOH·0.5CH₂Cl₂·H₂O (R = *tert*-butyl).

A number of heterobimetallic complexes containing bearing barium have been reported.^{23,24} For example, reaction of L⁶H₆ with Ba followed by [Ti(OiPr)₄]//TMEDA (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) in methanol led to the isolation of the complex {Ti(L⁶H₂)₂[Ba(MeOH)₂]₂}·3MeOH·1.25CH₂Cl₂ (**3**·3MeOH·1.25CH₂Cl₂). In the structure (CCDC 205214, Fig. 6), the three metals adopt a linear arrangement, and Ba π -arene interactions are evident. The L⁶H₂ ligands each adopt a 1,3-alternate conformation and houses a CH₂Cl₂ molecule in the cavity and exhibits C-H π -interactions.



Figure 6. Structure of $3 \cdot 3 \text{MeOH} \cdot 1.25 \text{CH}_2 \text{Cl}_2$ (R = *tert*-butyl, L = MeOH).

Group 3 metals

Scandium

Back in 2007, Shen *et al* reported the synthesis of a dark green product from the reaction of $[Sc(OiPr)_3]$ and $L^6H_6.^{25}$ Titration experiments indicated that the complex possessed 2.75% scandium, consistent with two OH groups of every six phenols coordinating to a scandium centre. The complex was employed for the ROP of 2,2dimethyltrimethylene carbonate in toluene, a process that was significantly affected by the temperature and the molar ratio. For example, increasing the temperature to 100 °C was favourable for the %conversion (28.4% at 40 °C *versus* 83.4% at 100 °C), however above 80 °C, the polymer molecular weight fell off suggesting that transesterification processes were in operation. Typical molecular weights at 80 °C were 33,000 Da with \oplus 1.21. Use of other solvents with larger dipole moments such as DMF, THF or acetonitrile led to significantly lower conversions, e.g. <10% in acetonitrile.

More recently, we have also investigated the interaction of $L^{6}H_{6}$ with scandium precursors.²⁶ We had most success when using the triflate [Sc(OTf)₃]. Reaction in DMSO/acetone in the presence of Et₃N led to the isolation of the complex [(L⁶)₂Sc₄(DMSO)₄]·2DMSO·2acetone (**4**·2DMSO·2acetone), (CCDC no. 2050783) in 38% yield. The molecular structure of **4**·2DMSO·2acetone was confirmed by X-ray diffraction, which revealed a centrosymmetric complex with a core in which five-coordinate trigonal bipyramidal scandium centres formed a central Sc₂O₂ square, see Fig. 7. This square formed the bridge between two L⁶ molecules, each of which bound to the square through three of their phenolic oxygen centres. The remaining

phenolic groups on each L^6 bind to an octahedral $\mathsf{Sc}(\mathsf{DMSO})_3$ fragment.

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Figure 7. Molecular structure of 4.2DMSO.2acetone.

Interaction of $[Sc(OiPr)_3]$ (two equivalents) with L^6H_6 in refluxing toluene also proved successful and following work-up in acetonitrile the complex $[(L^6H_4)Sc_2(OH)_2(NCMe)_2]_2$ ·12MeCN (5·12MeCN), CCDC (No. 2050785), was isolated in *ca*. 17% yield. The molecular structure (Fig. 8) revealed two fragments for which there are two asymmetric hydroxide bridges linking pseudo-octahedral scandium centres. The hydroxide bridges also each bind another scandium centre; the coordination of the latter scandium centres is completed by an acetonitrile ligand. To counterbalance the charge, four phenolic groups remain on each calix[6]arene ligand.

Cytotoxicity studies against the cancer cell lines HCT116 and HT-29 were conducted on the two scandium complexes and results revealed that for such a complex, the toxicity levels are acceptable for use in any subsequent polymer synthesis. The IC₅₀ values for **2**·2DMSO·2acetone where higher than those observed for **3**·12MeCN (Table 1), particularly against HCT116.

Agent	IC₅₀ (μM) HCT116	IC₅₀ (μM) HT-29
2·2DMSO·2acetone	11.27 ± 2.40	14.96 ± 1.37
3 ·12MeCN	2.36 ± 1.74	9.50 ± 1.26

Table 1. In vitro anti-cancer activity of scandium calix[6]arenes2·2DMSO·2acetone and 3·12MeCN.



Figure 8. Molecular structure of 5.12MeCN.

Group 4 metals

Titanium

Titanium was one of the first metals to be coordinated to calix[6]arene, for example back in 1986 Atwood *et al.* by reacting four equivalents of [TiCl₄] with L⁶(OMe)₆ were able to isolate and structurally characterize the complex {[(TiCl₂(OTiCl₃)]₂L⁶}. The L⁶ ligand adopted an elliptical cone conformation.²⁷ A year later, Calestani, Ungaro *et al.* also employed [TiCl₄], this time by reacting it with L⁶H₆ to afford the complex [(L⁶)Ti₂(μ -O)]₂, and although the X-ray data was of poor quality, it was clear that the structure comprised of two L⁶ ligands that sandwiched four distorted tetrahedral metal centres with two triply bridging oxygen centres completing the ladder-like motif.^{15a}

Later studies (2003) made use of one or two equivalents of $[Cp_2TiCl_2]$ with L⁶H₆/2KH to afford the complexes $[L^6H_3(TiCp)]\cdot CH_2Cl_2$ (**6**·CH₂Cl₂)/CCDC 202723 and $[L^6(TiCp)_2]\cdot CH_2Cl_2$ (**7**·CH₂Cl₂)/CCDC 202724 in high yield (*ca.* 90%). In such complexes (Fig. 9), L⁶ has an inverted cone conformation with a Cp group occupying one of the cavities.²⁸



Figure 9. Structure of 6. CH₂Cl₂ and 7. CH₂Cl₂.

In the years since, there has been significant work on titanocalix[4]arenes systems,²⁹ whilst work with L⁶ has mostly been restricted to our work on catalyst generation for ROP and work in China on oxygenation of sulfide *vide infra*. ³⁰⁻³² For example, in 2020 we treated L⁶H₆ with two equivalents of [TiCl₄] which, following work-up involving an extraction into acetonitrile, led to the isolation of the complex [Ti₂Cl₃(MeCN)₂(OH₂)(L⁶H)][Ti₂Cl₃(MeCN)₃(L⁶H)]·4.5 MeCN (**8**·4.5 MeCN) in 64% isolated yield. A molecular structure determination (CCDC 1973136) revealed two unique molecules in the asymmetric unit. One molecule possessed two titanium centres that were distorted octahedral and bound by either two chlorides, a water, an acetonitrile, a phenolic group from L⁶ and two phenoxides

of L⁶ or one chloride, two acetonitrile molecules and three phenoxides of L⁶. In the second molecule, the water molecule has been replaced by a chloride ligand. The molecules are linked via Hbonding which yields zig-zag chains along the b-axis. The confirmation adopt by L⁶ is twisted such that two small cups are formed; the structure is depicted in Figure 10.





Figure 10. Molecular structure of 8.4.5 MeCN.

We then treated L⁶H₆ with three equivalents of [TiF₄] and again using acetonitrile as the extraction solvent, we managed to isolate crystals of the complex $[(TiF)_2(\mu-F)L^6H]_2 \cdot 6.5 MeCN (9 \cdot 6.5 MeCN);$ isolated yield 68%. The structure (CCDC 2009076) comprised of two L⁶H ligands which each bind two pseudo-octahedral titanium centres and together form a core of two Ti₂F₂ diamonds. These diamonds link the two L⁶H molecules, whilst the fluorides link the metal centres and two further fluorides link the diamonds at each end (see Fig. 11).



Figure 11. Molecular structure of 9.6.5MeCN.

For the ROP of ϵ -CL, best results for 8.4.5MeCN were achieved when using the ratio [ϵ -CL]:[Ti]:[BnOH] of 250:1:3 at 130 °C over 24h, will led to 69% conversion and a polymer with molecular weight (M_n) 5240 and with good control (Đ 1.22). Use of 9.6.5MeCN led to no polymer. Similar observations were noted for the ROP of $\delta\text{-VL}$ and for r-LA. Complex 8.4.5MeCN was also capable of the

copolymerisation of ϵ -CL with δ -VL with a CL:VL ratio of about 40:60 in the copolymer.

L⁶H₆-derived complexes have also recently been exploited by other researchers for the oxidation of sulfides.^{31,32} This included the use of complexes [Ti₄O₂(L⁶)₂] (10) (CCDC No. 2226850), the ${Ti_2(L^6)(EtO)_2(SaH_2)_2}$ (SaH₂ = squaric acid) (11) (CCDC No 2226852), ${Ti_2(L^6)_2(EtO)_2(Oa)}$ (OaH₂ = oxalic acid) (12) (CCDC No 2226853), [H₂Ti₄(L⁶)(BA)₂(EtO)₁₀] (BAH = benzoic acid) (**13**) (CCDC No 2226854), (CCDC $[Ti_6O_2(L^6)(BA)_4(OiPr)_{10}]$ (14) No 2226855), [Ti₈(L⁶)₂(Sal)₄(EtO)₁₆] (**15**·*i*PrOH) (CCDC No. 2156021), [Ti₄(L⁶)₂(µ₃-O)₂(DMF)₂] (**16**·*i*PrOH) (CCDC No. 2156018) where for **11** – **15**, the titanium-oxo clusters where also supported by the presence of carboxylic acids (see Fig. 12).





















16∙*i*PrOH

Figure 12. Molecular structures of 10 - 16.

The solvothermal reaction of $[Ti(OiPr)_4]$ with L⁶H₆ in the presence of phenylphosphoric acid in DMF/iPrOH/CHCl₃ led to the isolation of the complex $[Ti_8(L^6H_3)_4(C_6H_5PO_3)_8(\mu_2-O)_4]^{4-}$ (**17**·2CH₂Cl₂) in *ca*. 68% yield.³² The structure (CCDC 2156019, Fig. 13) is best described as a windmill, with the L⁶H₃ ligands bound to the Ti₄ ring adopting an 'up-down' double partial cone conformation. The Ti₄ core is also supported by a phenylphosphoric acid ligand which binds to two of the titanium centres (and also binds to an adjacent 'outer' Ti centre).



Figure 13. Molecular structure of 17.

Other studies have also focussed on the use of $L^{6}H_{6}$ -derived species for the photocatalytic cycloaddition of carbon dioxide to epoxides.³³ The complexes involved (see Fig. 14) were $[Ti_4(\mu_3-O)_2(L^6)_2(CH_3CN)_2]$ ·MeCN (**18**·MeCN) (CCDC No. 2344847) and $[Ti_{28}(\mu_2-O)_{18}(\mu_3-O)_{18}(L^6)(PA)_{34}(iPrO)_2]$ ·4MeCN (PA = propionic acid) (**19**·4MeCN) (2344848).



Figure 14. Molecular structures of 18 (left) and 19 (right).

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Given the flexibility exhibited by L⁶H₆ in the titanium-catalysed ROP chemistry described earlier in this section, we decided to investigate how changing the linker might further help to develop the possible coordination chemistry available. The macrocycle p-tertbutyltetrahomodioxacalix[6]areneH₆ (L^{6dioxo}H₆, Fig. 1, middle), which contains two dimethyleneoxa linkages is readily available in good vield,³⁴ looked to be an ideal candidate for further investigation. On reaction with excess (three equivalents) [Ti(OiPr)₄], and following work-up in acetonitrile, the complex [Ti₂(O*i*Pr)₂(MeCN)L^{6dioxo}]·3.5MeCN (**20**·3.5MeCN) was isolated in 52% yield. In the structure (Fig. 15, CCDC No. 2057320), there are two titanium centres, one has a slightly distorted rectangular pyramidal geometry and the other has an additional bound acetonitrile and so is distorted octahedral. Conducting the reaction with two equivalents of $[Ti(OiPr)_4]$ and in the presence of adventitious water/oxygen lead to the formation of a Ti₄O₄ ladder-like structure $[Ti_4(\mu_3-O)_2(H_2O)(L^{6dioxo})_2]$ ·MeCN (**21**·MeCN) (Fig. 16, CCDC No. 2057321).



Figure 15. Molecular structure of 20.3.5MeCN (L = MeCN).



Figure 16. Molecular structure of 21 · MeCN.

ROP studies using ε -CL, δ -VL and *r*-LA were conducted using these two dioxacalix[6]arene complexes using the optimized conditions of 250:1 for [monomer]:[cat] in the presence of one equivalent (per Ti) of BnOH; in the absence of BnOH, conversions were lower. The molecular weights (M_n) of the obtained polymers were much lower than the calculated values, though the small D values (<1.75) were suggestive of reasonable control. MALDI-ToF spectra indicated that polymers with end groups H/OH and H/OBn were formed. Complex **20** also exhibited appreciable activity when used under air. A kinetic study revealed the rate order **21** > **20**; the same trend was observed for polyvalerolactone (PVL) under similar conditions. MALDI-ToF spectra of the PVL indicated that both linear polymers with H/OBn end groups and cyclic polymers were present. For *r*-LA, **21** again

performed best and afforded polymers with a syndiotactic bias; *Pr* values suggested near heterotactic polymers. Both complexes were also capable of the copolymerisation of *r*-LA with ε -CL, however neither complex proved capable of the ROP of ω -pentadecalactone under the conditions employed.

We then turned our attention to the use of aza (-CH₂-N(Me)-CH₂-) type bridges, macrocycles for which very little coordination chemistry has been reported.³⁵ We chose as our entry point *p*-methyl-dimethyldiazacalix[6]areneH₆ (L^{6diaza}H₆, Fig. 1, right), which on reaction with [TiF₄] (four equivalents) led to the isolation of the complex [Ti₄F₁₄(L^{6diaza}H₂)(H)₂]·2.5MeCN (**22**·2.5MeCN, Fig. 17) in 56% yield. The structure (CCDC No. 2057322) revealed a central Ti₄F₁₄ core containing distorted octahedral metal centres, all linked via fluoride bridges. L^{6diaza}H₂ only binds in adjacent bidentate *O*,*O*-fashion to two of the metal centres; the coordination at the other two metals is fluoride based only.



Figure 17. Molecular structure of 22.2.5MeCN.

Use of $[TiCl_4(THF)_2]$ (two equivalents) or $[TiBr_4]$ (four equivalents) in place of $[TiF_4]$ led to the isolation of complexes of formula $[Ti_2X_4(H_2O)_2O(L^{6diaza}H_2)(H)_2] \cdot nMeCN$ (**23** X = Cl, n = 5MeCN; **24** Br, 4·5MeCN), Fig. 18. The isostructural complexes (CCDC No. 2057323) and CCDC No. 2057324) contain two distorted octahedral metals centres that are linked via a near linear oxo bridge (168.84(6)° for **23**, 172.65(17)° for **24**).



Figure 18. Molecular structures of 23.5MeCN and 24.4.5MeCN.

Use of excess [TiBr₄] (> four equivalents) led to the complex $[Ti_4Br_{12}(L^{6diaza})(H)_2(MeCN)_6]$ ·7MeCN (**25**·7MeCN) (CCDC No. 2057325, Fig. 19) in 26% yield. $L^{6diaza}H_2$ binds to two of the metal centres in

bidentate O,O-fashion (but not adjacent phenoxides as in **22**), and in monodentate fashion to the other two metal centres present. $L^{6diaza}H_2$ twists significantly to accommodate the metals such that the monodentate bound metals appears on opposite side of the $L^{6diaza}H_2$ plane.



Figure 19. Molecular structure of 25.7MeCN.

For ROP studies using ε -CL, δ -VL and *r*-LA, these aza complexes were less active than the oxacalix[6]arene complexes **20** and **21**. They did though outperform the related titanium azacalix[4]arene complex $[Ti_2F_2(\mu-F)_3L^{aza4}(H)_2(SiF_5)]\cdot 2MeCN$ where $L^{aza4}H_4 = p$ -methyldimethyldiazacalix[4]areneH₄).³⁴

Group V metals

Vanadium

Vanadium is another metal that was subject to some of the earlier studies into metal calixarene coordination chemistry. In terms of calix[6]arene work, we treated L⁶H₆ with [V(NtBu)(OtBu)₃] and, following work-up using THF/MeCN, isolated the complex {[V(NtBu)(THF)_{0.39}(tBuOH)_{0.61}]VO(μ -O)₂L⁶}[tBuNH₃]·2MeCN (**26**·2MeCN), Fig. 20. A molecular structure determination (CCDC No. 155488) using synchrotron radiation revealed a severely twisted L⁶ conformation to accommodate the three vanadium centres. Two of the metal centres are tetrahedral whilst the 'central' vanadium adopts an octahedral arrangement. The metals are arranged such that the two vanadyl groups and the imido ligand all point roughly in



Figure 20. Molecular structure of the anion in 26.2MeCN.

the same direction on the same side of L⁶.³⁶

Our next venture into vanadium calix[6]arene chemistry involved the use of the heterobimetallic starting material Li[VO(OtBu)₄], generated *in-situ* from [VOCl₃] and four equivalents of LiOtBu.³⁷ Use of two equivalents of Li[VO(OtBu)₄] with L⁶H₆ afforded the complex [Li(MeCN)₄][V₂(O)₂Li(MeCN)(L⁶H₂)₂]·8MeCN (**27**·8MeCN) in about 65% yield. In the structure (Fig. 21, CCDC No. 895364), the two L⁶H₂ ligands each coordinate to two distorted squared-based pyramidal vanadyl centres; for the latter, the oxygen centres are linked via an Li(NCMe) which is also bound to a phenolic group of L⁶.



Figure 21. Molecular structures of **27**·8MeCN and **28**·9.67MeCN (which differ only in the amount of solvent present).

In separate reaction, the related complex а $[Li(MeCN)_4][V_2(O)_2Li(MeCN)(L^6H_2)_2]$.9.67MeCN (28.9.67MeCN) (CCDC No. 950038), differing only in the amount of solvent of crystallization, was isolated. From this reaction, a second product which was formed in much lower yield (ca. 10%) was found to have the formula $\{[(VO_2)_2(L^6H_2)(Li(MeCN)_2)_2]\cdot 2MeCN\}_n$ **29**·2MeCN. The overall structure (Fig. 22, CCDC No. 950039) adopted was that of a 1D polymer formed via Li₂O₂ and L⁶H₂ units. The distorted tetrahedral vanadyl groups help form the link between the calix[6]arene and the Li₂O₂ motif. The L⁶H₂ ligand adopts a chair conformation.



Figure 22. Molecular structure of 29.2MeCN.

We then explored how first lithiating the calix[6]arene using LiOtBu (seven and a half equivalents) and subsequently treating it with a vanadyl reagent, namely [VOCl₃] (two equivalents) would affect the outcome. Work-up in THF led to the isolation of the complex $[VO(THF)][VO(\mu-O)]_2Li(THF)(Et_2O)][L^6]]\cdot 2Et_2O\cdot 0.5THF$

(**30**·2Et₂O·0.5THF, Fig. 23) (CCDC No. 1027898) in *ca*. 46% isolated yield. The trinuclear motif at the core comprised a central octahedral metal flanked by two tetrahedral metals supported by the calixarene in this structure and resembles that seen in the dioxo-*tert*-butylimido complex mentioned above. The conformation adopted by L⁶ is best described as 'down, down, down, out, out'.



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Figure 23. Molecular structures of **30**·2Et₂O·0.5THF and **31**·Et₂O·2THF (which differ only in the amount of solvent present).

In a separate reaction, but under the same conditions, the amount of LiOtBu employed was increased to 15 equivalents. The product isolated turned out to be the same differing only in the amount of solvent of crystallisation, *i.e.* {[VO(THF)][VO(μ -O)]₂Li(THF)(Et₂O)][L^c]}·Et₂O·2THF (**31**·Et₂O·2THF) (CCDC No. 1027899).

As for titanium, our calix[6]arene studies with vanadium were extended to include the dimethyleneoxa bridged system $L^{6dioxa}H_{6.}^{38}$ Interaction with Na[VO(tBuO)4] led, following work-up in acetonitrile, to the complex [(VO)2(μ -O)Na2(L^{6dioxa})(MeCN)4]·5(MeCN) (**32**·5MeCN, Fig. 24) in 34% isolated yield. Within the structure (CCDC No. 1998549), a near linear [171.8(2)°] oxo bridge links two trigonal bipyramidal vanadyl centres. An Na(NCMe)2 fragment binds to each of the dimethyleneoxa bridges as well as to two of the phenolate oxygen centres.



Figure 24. Molecular structure of 32.5MeCN.

If $[VO(OnPr)_3]$ is employed as the entry point, then the product isolated is the tetra-vanadyl complex $\{[VO]_4(L^{6dioxa})\}$ ·6MeCN) (**33**·6MeCN) (CCDC No. 1998550, Fig. 25). The vanadyl groups along with oxo groups form a 4-step ladder. Two of the vanadium centres are distorted octahedral and are involved in bonding to the L^{6dioxa} bridges, whilst the other two metal centres adopt trigonal bipyramidal geometries.



Figure 25. Molecular structure of 33.6MeCN.

It proved possible to isolate a family of imido complexes incorporating L^{6dioxa} via the use of the precursors [V(Np- $C_{6}H_{4}Rp)(OR')_{3}]$ (R = Me (34·4MeCN·CH₂Cl₂), OMe (35·4MeCN), CF₃ (36), Cl (37), F (38·7MeCN); R' = tBu, iPr, nPr or Et). These complexes (CCDC No. 1998551 Me, 1998552 OMe, 1998553 CF₃, 1998554 Cl; the structure of 38 was not determined via crystallography) all adopt a dimeric structure containing two square pyramidal vanadium centres linked via asymmetric aryloxide bridges derived from L^{6dioxa}. The p-CF₃ derivative 36 is shown below (Fig. 26).



Figure 26. Molecular structure of 36.

These oxacalix[6]arene vanadium species proved to be active, with and without BnOH present, for both the ROP of ε -CL and of δ -VL, plus, the copolymerisation thereof. In the case of the imido family, in the presence of BnOH, kinetics revealed the activity order (CF₃) > (Cl) > (F) > (OMe) > (Me) for both ε -CL and δ -VL, *i.e.* electron withdrawing substituents favour high activity. A number of smaller oxacalixarenes as well as traditional methylene-bridged species were tested under the same conditions, and it was found that the L^{6dioxa} derived systems were more active, which was attributed to the flexibility of L^{6dioxa}. Products tended to be of low molecular weight but were formed with reasonable control ($D \le 1.68$ for ε -CL; ≤ 1.76 for δ -VL).

For the copolymerisation of ε -Cl with δ -VL, best activity (>70%) was observed for 32.5MeCN, whilst 36 also exhibited appreciable activity (>60%). The systems revealed a preference for CL incorporation and revealed a 'blocking' tendency with a number average sequence length of 7.17 (CL) and 5.30 (VL) with a randomness degree R of 0.33. The imido family were subject to ethylene polymerisation screening in the presence of either dimethylaluminium chloride (DMAC) or diethylaluminium chloride (DEAC) and ethyltrichloroacetate (ETA). DMAC proved to be the co-catalyst of choice, and the activity trend 34 (p-Me) \approx 36 (p-CF₃) > 38 (p-F) > 37 (p-Cl) > 35 (p-OMe) was observed. High catalytic activities were achieved, of the order of 0.9-1.5 x 10^7 g PE (molV)⁻¹ bar⁻¹h⁻¹, which was maintained for about 20 mins, and in each case highly linear polyethylene was formed. The oxo complex 32.5MeCN together with the imido complexes 34- 38 were also screened as catalysts for the co-polymerisation of propylene oxide and CO₂ to form cyclic/polycarbonates.³⁹ The imido compounds turned out to be either inactive or very poor catalysts

(TON = $0 - 0.055 \text{ g/g}_{cat}$), whilst only a slightly better performance was afforded by 32.5MeCN (TON 1.523 g/gcat).

Interestingly, the L^{6dioxa}H₆ macrocycle can be cleaved during reaction with the imido precursors, and from such a reaction we were able to isolate and characterize the complex $[VO(L^{\rm 6cleaved})]_2{\cdot}4MeCN$ (39.4MeCN) (L^{6cleaved} = 2-(p-CH₃-C₆H₄NCH)-4- tert-Bu-C₆H₂O-6-CH₂)-4tert-BuC₆H₂OH), Fig. 27. In the structure (CCDC No. 1998555), it is clearly seen that a new metallomacrocycle containing two squaredbased pyramidal vanadyl centres is formed.



Figure 27. Molecular structure of 39.4MeCN.

Niobium

We extended our group V studies to the use of [NbCl₅], and found that on interaction with L⁶H₆, and following work-up in acetonitrile, the complex [{Nb(NCMe)Cl₂}(L⁶)]·2MeCN (40·2MeCN) (CCDC No. 624576), was isolated in ca. 66% yield. Use of synchrotron radiation revealed how the L⁶ had twisted to accommodate the two niobium containing fragments forming two small cups in the process (each utilizing three phenolate groups), Fig. 28. One cup has 'captured' a solvent (MeCN) molecule, and this is reflected in the ¹H NMR spectrum where an MeCN peak is found at δ = 0.35 ppm (*i.e.* shielded). It is worth noting that at ambient temperature, the NMR peaks are broad but cooling down to 273K allows for sharpening of the peaks and assignment via the use of double quantum-filtered (DFQ) COSY experiments and homonuclear 2D J-resolved experiments. In the structure, one distorted octahedral niobium (bearing cis-chlorides and an MeCN) is above and one below the L⁶ plane.40



Figure 28. Molecular structure of 40.2MeCN (R = tBu).

If the [NbCl₅] is replaced by [NbOCl₃] then the reaction conducted under the same conditions affords both 40 and the complex [$Nb_2(\mu$ -O)₂(μ -Cl)(L⁶H)}₂·16MeCN (**41**·16MeCN, Fig. 29) in an isolated ratio of about 1.5:1. The IR spectrum of this minor complex contained bands associated with both vNb-O-Nb (600 - 800 cm⁻¹) and vNb-OH (3150 cm⁻¹) bonds. In the structure (CCDC No. 624578), the L⁶H ligands each coordinate to two distorted octahedral niobium centres, and each half of the molecule is linked at the niobium centres by μ_2 -bridging chloride and oxo ligands. The two L⁶H ligands adopt an enlarged-like conformation which is slightly twisted.



Figure 29. Molecular structure of 41.16MeCN.

The complex **40**·2MeCN was screened for its potential to act as a catalyst for the polymerisation of ethylene in the presence of a variety of organoaluminium co-catalysts and the re-activator ethyltrichloroacetate (ETA). When either methylaluminoxane (MAO) or trimethylaluminium were employed, the catalytic activity was near zero, whereas use of dimethylaluminium chloride (DMAC) or diethylaluminium chloride (DEAC) led to increased activity. These activities were still poor (<50 g mmol⁻¹h⁻¹bar⁻¹) though it was possible to identify the products as high molecular weight linear polyethylene (e.g. M_W = 319,000 Da with D = 2.4).

Tantalum

As for niobium, the use of 2.2 equivalents of the pentachloride resulted in an isostructural twisted structure **42**·2MeCN (CCDC No. 624577, Fig. 30) accommodating two metal dichloride acetonitrile fragments [{Ta(NCMe)Cl₂}(L⁶)]. In this case, it proved possible to increase the yields by employing dichloromethane as reaction solvent rather than toluene. In the IR spectrum, peaks for both free and bound MeCN were evident at 2340 and 2295 cm⁻¹, respectively.



Figure 30. Molecular structure of $42 \cdot 2 \text{MeCN}$ (R = *t*Bu).

In ethylene polymerisation studies, this tantalum system exhibited comparable activities to those observed for the isostructural niobium complex with similar control, though the polymers isolated possessed lower molecular weights (e.g. M_W = 167,000; D = 2.5).

Chromium

Our attempts to use group VI metallocalix[6]arenes as polymerisation catalysts have been met with little success. For example, the chromium(III) complex [Cr(L⁶H₃)Na(MeCN)₂(μ -OH)]₂·4MeCN (**43**·4MeCN) (CCDC No. 697243, Fig. 31), formed via the interaction of L⁶H₆ with Na[Cr(OtBu)₄], proved to be of very low activity when employed alongside DMAC or MAO for the polymerisation of ethylene.⁴¹



Journal Name

Figure 31. Molecular structure of 43.4MeCN (L = MeCN).

Molybdenum

Studies of molybdocalix[6]arene chemistry are very limited, but include the exploration of molybdenum imido chemistry by reacting $\{Mo(OtBu)_2[2,2'-(N)-C_6H_4]_2(CH_2CH_2)\}\$ which, after undergoing a ring opening reaction in the presence of L⁶H₆ and releasing a pendant amino group, underwent an insertion reaction involving a metal bound acetonitrile to afford the complex [Mo(2-NC_6H_4CH_2CH_2C_6H_4NHC(Me)NH-2')L⁶H_2]·4MeCN (44·4MeCN) (CCDC No. 146026, Fig. 32). The conformation adopted by the L⁶H₂ here is a rare example of a humped-like structure.⁴²



Figure 32. Molecular structure of $44 \cdot 4$ MeCN (R = *t*Bu).

The methodology (*i.e.* loss of *tert*-butanol) was extended to hydrazido(2-) chemistry, whereby L⁶H₆ and [Mo(NNPh₂)(OtBu)₂] were combined to afford {[Mo(NNPh₂)]₂(μ -O)L⁶} (**45**·4MeCN) (CCDC No. 162064, Fig. 33). The enlarged cup conformation of L⁶ here supports a confacial bioctahedral core formed by the two molybdenum centres.⁴³



Figure 33. Molecular structure of 45.4MeCN.





Studies on tungsten involved the use of [WOCl4] which led to the complex [(WOCl2)2L⁶H2] (46.8MeCN) (CCDC No. 203411) for which

the L^6 adopts a pinched conformation to accommodate the two facially bound metal centres (Fig. 34).⁴⁴



Figure 34. Molecular structure of 46.8MeCN.

In terms of catalysis, we have investigated the use of $[W(eg)_3]$ (eg = 1,2-ethanediolato) as a means of entry in tungstocalix[6]arene chemistry.⁴⁵

Use of 1 or 2 equivalents of $[W(eg)_3]$ (eg = 1,2-ethanediolato) led to the oxo-bridged complex { $[W(eg)]_2(\mu-O)L^6$ } **47** (CCDC No. 989342, Fig. 35), in which a near linear (164.7(6)°) oxo bridge links two distorted octahedral tungsten centres. The conformation adopted by L⁶ is an enlarged cup.



Figure 35. Molecular structure of 47.

Increasing the amount of $[W(eg)_3]$ to four equivalents led to the isolation of $\{[W(eg)_2]_2L^6H_2\}\cdot 2MeCN$ (**48** · 2MeCN) (CCDC No. 1010285) in *ca*. 45% yield. Again, the tungsten centres are distorted octahedral (Fig. 36) and are each bound by two eg ligands and two phenoxide oxygens of L⁶; the latter adopts a large cup conformation.



Figure 36. Molecular structure of 48.2MeCN.



Figure 37. Molecular structure of 49.0.83toluene MeCN.

The complexes **47-49** were evaluated for their potential to act as catalysts for the ROP of ε -CL in the presence of BnOH at 110 °C. Interestingly, the data revealed that use of either L⁶H₆ or L^{6dioxa}H₆ afforded >80% conversion, whereas related calix[8]arene systems proved to be inactive under the same conditions. MALDI-ToF spectra revealed the presence of chain polymers with H/OBn end groups.

Group 8 metals

Iron

Of these metals, iron has in recent years attracted much interest given its recent history for both α -olefin polymerisation and for the ROP of cyclic esters.⁴⁶ In terms of work done with L⁶H₆, this has focussed mostly on systems with the potential to be used as ROP catalysts. Back in 2010, we explored the use of the heterobimetallic reagent [MFe(OtBu)₃(THF)]₂ (M = Na, K), which on interaction with L₆H₆ afforded the iron(III) complexes with the formulae {[Fe₂(μ -O)Na₂(OH₂)(NCMe)₂L⁶]₂}{[Fe₂(μ -

O)Na(OH₂)(NCMe)₆L⁶]₂}Na(NCMe)₅]₂·9.46MeCN (**50**·9.46MeCN) (CCDC No. 749031: and $[{Fe_2(\mu-O)L^6(K(NCMe)_2)_2}_2]$ ·10.8MeCN (**51**·10.8MeCN), respectively (Fig. 38).⁴⁷





Figure 38. Top: The molecular structure of **50**·9.46MeCN (chem draw is the neutral complex; (Na(NCMe)₂ fragments are missing in the anionic species); bottom: proposed neutral structure in **51**·10.8MeCN (K(NCMe)₂ fragments are missing in the anionic species).

The formula of **50**·9.46MeCN highlights just how complex these systems can be given that a cation, anion and a neutral molecule all appear in the one complex. The structure of **51**·10.8MeCN resembles that of the anion of **50**·9.46MeCN, and both contain a tetra-ferric ladder-like structure sandwiched between two cone-like L⁶ ligands. Mössbauer spectra were consistent with the presence of high spin iron(III), whilst magnetic susceptibility measurements yielded a μ eff of 5.5 μ B. Complex **51**·10.8MeCN was formed in *ca*. 60% yield, and was formed alongside a minor product (*ca*. 10%) having the formula {[(L⁶)₂Fe₈O₈][K(MeCN)_{1.5}K(H₂O)(MeCN)_{2.5}]₂}·6MeCN (**52**·6MeCN). In the structure (Fig. 39, CCDC No. 749032), the {[(L⁶)₂Fe₈O₈] form chains via bridging K+ ions.



Figure 39. Molecular structure of 52.6MeCN.

The ROP behaviour of **50**·9.46MeCN and **51**·10.8MeCN was examined toward ε -CL, and at room temperature conversions of *ca*. 80% were achievable over 40h in the presence of one equivalent of benzyl alcohol. The isolated products were of low molecular weight (M_n <2000 Da) which suggested significant back biting reactions (transesterification) during the ROP.

For comparative studies, the complexes $[Na_2(CH_3CN)_4(L^{6dioxo})Fe_2(\mu-O)]$ (M=Na **53**·4(CH_3CN), K **54**·2(CH_3CN)) were prepared via the use of $[MFe(OtBu)_3(THF)]_2$ (M = Na, K). In these near isostructural complexes (CCDC No. 749034, 749035 see Fig. 40, the double cone conformation adopted by L^{6dioxo} supports a bent Fe-O-Fe linkage (133.3(4) Na, 133.95(12) K), flanked either side by M(NCMe)_2 fragments that are each bound to two oxygen centres of L^{6dioxo} . ROP studies failed to reveal any beneficial effect from the presence of the dimethyleneoxa bridges.



Figure 40. Molecular structure of $[Na_2(CH_3CN)_4(L^{6dioxo})Fe_2(\mu-O)]$ (M=Na 53·4(CH_3CN), K 54·2(CH_3CN)).

Group 9 metals

Our interest here has been mostly with cobalt species and we have looked at these as potential catalysts for water splitting.⁴⁸ The initial entry was via the lithiated Li₁₄ species **1** formed on treatment of L⁶H₆ with LiOtBu followed by subsequent treatment with CoBr₂ (two

equivalents) and work-up in acetonitrile. This resulted in the isolation and structural characterization of the complex ${(L^6CoLi_4(MeCN)_2(tBuO)(H_2O)CoBr_2(L^6Co(H_2O)Li_5(MeCN)_4(THF))\cdot 15 MeCN (55.15MeCN) (CCDC No. 2090095). The structure (Fig. 41) is$ $quite unusual and involves two metalated (CoLi_4 or CoLi_5) L^6$ $fragments which are bridged by a CoBr_2 unit.$



Figure 41. Molecular structure of 55.15MeCN (L = MeCN).



Given the complexity of the above product, an alternative route was employed using NaH (six equivalents followed by the addition of CoBr₂ (three equivalents)). The result was the complex [Co₆Na(NCMe)₆(μ -O)(L⁶H)₂Br]·7MeCN (**56**·7MeCN) (CCDC No. 2152001) which was isolated in 70% yield. This complex (Fig. 42) possesses a central trigonal prismatic core and an addition cobalt and sodium ion all of which help link together the two unique L⁶ ligands.



Figure 42. Molecular structure of 56.7MeCN (L = MeCN).

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In terms of electrocatalysis, of these two cobalt species only **56**·7MeCN was subject to rigorous analysis as **55**·15MeCN proved to be electrochemically unstable over the operating range employed. For **56**·7MeCN, the oxidation appeared quasi-irreversible, whilst it was catalytic activity toward electrochemical proton reduction was demonstrated *versus* the reference CoCl₂, with the catalysis occurring homogenously. Data associated with the mass transfer coefficient, charge transfer resistance and current magnitude at the catalytic turnover all suggest this complex has potential as a molecular catalyst for electrochemical proton reduction.

It is noteworthy that use of L⁶H₆ versus L^{6dioxo}H₆ on reaction with Co(NO₃)₂ in DMF results in very different structures (Fig. 43) with L⁶ forming a coordination polymer of formula [Co(L⁶H₂)(DMF)₃]·(DMF)₃ (**57**·3DMF), CCCD: 891015: catena-(tris(*N*,*N*-dimethylformamide)-(μ_2 -5,11,17,23,29,35-hexa-tert-butyl-37,40-dioxy-38,39,41,42-

tetrahydroxycalix[4]arene)-cobalt(II) N,N-dimethylformamide solvate). By contrast, L^{6dioxo}H₆ forms the complex [Co(L^{6dioxo}H₂)(DMF)₃(H₂O)]·(DMF)·2.5(H₂O) (**58**·2.5H₂O); CCDC 891015. In the polymer, bridging is via cobalt centres linked to a phenolate oxygen of adjacent molecules of L⁶H₂, with the latter adopting a double partial cone conformation. In the complex, the L^{6dioxo}H₂ possesses a double cone confirmation, and coordination of an oxygen from one of the dimethyleneoxa bridges help to stabilize the system.⁴⁹





Figure 43. Molecular structures of 57.3DMF and 58.2.5H2O.

Group 12

Zinc

A zinc complex of $L_{6dioxo}H_6$ has been reported (Fig. 44), namely $[L^{6dioxo}(ZnEt)_4Zn_2(CH_3CN)_4(\mu-OEt)_2]\cdot 2MeCN$ (59.2MeCN) (CCDC No. 749037) prepared via the use of EtzZn (six equivalents). The fully

deprotonated L^{6dioxo} supports a 4-step Zn-O ladder containing two tetrahedral zinc centres and two distorted trigonal bipyramidal zinc centres. Two other tetrahedral zinc centres are bound to the L^{6dioxo}, one either side of the ladder.⁴⁷



Figure 44. Molecular structure of 59.2MeCN.

In ROP studies, this zinc complex with ε -CL achieved a conversion of 43% at 60 °C over 24h. The catalyst can operate at low loadings, but polymer molecular weights suffered from back biting and so were significantly less than calculated values.

Main group elements

Of the limited examples of main group calix[6]arenes, an early example is worthy of mention here. Interaction of L^6H_6 with Me₃Al, with work-up involving addition of THF resulted in the formation of the complex



Figure 45. Molecular structure of 60.2THF.0.5toluene.



Group 14



There is a lack of structural information concerning lead calixarenes and given recent reports showing the potential of lead catalysts for ROP, we embarked on a study of lead calixarene chemistry.⁵¹ In the case of L⁶H₆, we utilized the starting materials [LiPb(OiPr)₃]₂ and {Pb[N(TMS)₂]}, which following work up in acetonitrile, led to the isolation of the complexes [Pb8Li10Cl2(L⁶H2)3(L⁶)(OH)2(O)2(H2O)2(MeCN)4]·14MeCN (**61**·14MeCN) (47% yield) and [Pb10Li2(L6)2(OH)Cl(O)4]·9.5MeCN (62·9.5MeCN) (46% yield), respectively. The structure (CCDC No. 2102470) of 61·14MeCN involves three doubly protonated L⁶H₂ ligands and an L⁶ ligand and has at its core a diamond-like Pb2O2 structure which is linked via several oxo bridges to other Pb and Li centres, see Fig. 46. In the case of 62.9.5MeCN (CCDC No. 2102473) the core comprises a Pb10Li2

centrosymmetric cluster with each L⁶ binding five Pb centres and Li centres linked via hydroxo/oxo and chloride bridges (Fig. 47). The presence of the chloride is a result of the *in-situ* generation of {Pb[N(TMS)₂]} from PbCl₂/(Me₃Si)₂NH/nBuLi.





Figure 46. Molecular structure of 61·14MeCN (L = MeCN).





Figure 47. Molecular structure of 62.9.5MeCN.

Both lead complexes were screened for their ability to act as catalysts in the ROP of ε -CL, δ -VL and *r*-LA at 130 $_{\circ}$ C, with or without benzyl alcohol present and over 8 or 24h; complex **61**·14MeCN outperformed **62**·9.5MeCN in terms of conversion. However, both complexes outperformed the reference compounds [Pb(OiPr)₂] and {Pb[N(SiMe₃)]₂}. The molecular weights (M_n) of the polymers obtained were also larger when employing **57**·14MeCN, for example when using ε -Cl/BnOH/**61**·14MeCN at 130 °C M_n = 11.25 x 10₃ Da *versus* 4.89 x 10³ Da for **62**·9.5MeCN. The enhanced activity of **61**·14MeCN was thought to be due to the presence of the lithium centres and/or labile MeCN ligands. For both PCL and PVL, the process involved an induction period, whilst for the polymer products the MALDI-ToF spectra revealed the presence of multiple families including H/OH and H/OBn end groups. The lower than calculated molecular weights suggested extensive transesterification was occurring during the ROP process, whilst NMR/MALDI-ToF spectra were consistent with a coordinative insertion mechanism. The systems were also capable of the copolymerisation of ε -Cl with δ -VL, with **61**·14MeCN affording *ca*. 70% conversion (*versus ca*. 40% for **62**·9.5MeCN); complex **62**·9.5MeCN showed a preference for VL incorporation (55%).

For PLA synthesis, the activities of $[Pb(OiPr)_2]$ and $\{Pb[N(SiMe_3)]_2\}$ were similar to **61**·14MeCN and greater than observed for **62**·9.5MeCN (when **61**·14MeCN and **62**·9.5MeCN were employed in the presence of BnOH). 2D *J*-resolved NMR spectroscopy revealed a syndiotactic bias, whilst the observed *P*r values (0.39-0.61) were consistent with near heterotactic polymers.

We also prepared a lead complex of L^{6dioxa}H₆ by interaction of this macrocycle with [Pb(*OiP*r)₂] (five equivalents). The product from this reaction turned out to be a large structure **63**·11MeCN (CCDC No. 2102471) comprising thirteen unique lead centres (Fig. 48). The arrangement was such that one cluster of nine lead centres together with four oxides were sandwiched between two L^{6dioxa} ligands, whilst off to the side and linked *via* an oxygen is a smaller cluster of four lead centres surrounding a central oxo and supported by a third L^{6dioxa} ligand. The overall formula is [Pb13(L^{6dioxa})₃O₄(*i*PrOH)]·11MeCN (**63**·11MeCN). For the ROP studies, kinetic studies for the PCL/PVL runs revealed the order **61**·14MeCN > **63**·11MeCN > **62**·9.5MeCN, with first order dependence; lead calix[8]arenes screened under the same conditions were less active. For the *r*-LA ROP, **63**·11MeCN performed the poorest with only *ca*. 25% conversions and afforded low molecular polymers.



Figure 48. Molecular structure of 63-11MeCN.

Lanthanides and Actinides

The chemistry of calixarene lanthanide chemistry has recently been reviewed.⁵² Actinide chemistry is somewhat limited, though a significant amount of work has been done with uranium. During such studies, the increased effectiveness of calix[6]arene-based systems (*versus* other calixarenes) for U(VI) separation has been noted.⁵³

Conclusions

The outputs described in this perspective underline the ability of the calix[6]arene system to support exciting, novel structural motifs. In some cases, it has been shown that calix[6]arene ligation promotes catalysis whilst other calixarenes do not. This may be attributed to conducive metal-metal distances and/or favourable calixarene conformations. Moreover, there is currently much interest in multinuclear (both homo- and hetero-nuclear) based catalysts, and it is clear from the structures described herein that calix[6]arene is an ideal scaffold for supporting such catalysts. Studies of structure/activity relationships have the potential to identify the optimum metal-metal separation distances as well as the number and type of metals required for specific metallocalix[6]arene catalysed processes. There is also the potential to control the type of polymer formed by 'capping' the calixarene at one rim, thereby forcing the monomer to approach in a specific direction/orientation akin to heterogeneous catalytic surfaces. To-date, much work has been done with the more established calix[6]arene (L⁶H₆) macrocycle, whilst recent advances have tended to utilize newer additions such as oxacalix[6]arenes (-CH2OCH2- bridges; e.g. L^{6dioxa}H6) and azacalix[6]arenes (-CH_2NMeCH_2- bridges, e.g. $L^{6diaza}H_6).$ This is likely to continue as synthetic methodologies improve and new pathways are discovered for the functionalization of such macrocycles. Indeed, such studies on oxa- and aza-type calix[6]arenes offer the possibility of exploiting the properties of hemi-labile functionality at the calixarene bridge. The observed cleavage in the case of the aza ligand set may also pave the way to other useful compounds that can be exploited as new chelates in catalysis.

Data availability

No primary research results, software or code have been included. For analysis of crystal structures, crystallographic data from the CCDC has been used.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

CR thanks the EPSRC for funding (EP/X01374X/1).

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Appendix

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CSD nomenclature of the parent calixarenes and complexes discussed in this perspective:

 $\label{eq:L6H6} L^6H_6\cdot 1.5MeCN:\ CCDC\ No.\ 215817:\ 5,11,17,23,29,35-hexa-tert-butyl37,38,39,40,41,42-hexahydroxycalix[6]arene \ acetonitrile clathrate acetonitrile solvate.$

1·14THF: bis(μ-5,11,17,23,29,35-hexa-*tert*-butyl-37-hydroxy-38,39,40,41,42-pentaoxidecalix[6]arene)-bis(μ-carbonato)-

tetrakis(μ -aqua)-diaquahexakis(tetrahydrofuran)tetradecallithium tetrahydrofuran solvate.

2·7*i*PrOH·0.5CH₂Cl₂·H₂O: bis(µ₂-5,11,17,23,29,35-hexa-*tert*-butyl-37,38-dihydroxycalix[6]arene-39,40,41,42-tetraolato)-

aqua-tris(isopropoxy)-di-strontium-titanium(IV)

tetrakis(isopropanolate) dichloromethane solvate

methanol solvate **4**·2DMSO·2acetone: bis(μ-5,11,17,23,29,35-hexa-*t*α

4·2DMSO·2acetone: bis(μ-5,11,17,23,29,35-hexa*-tert*butylcalix[6]arene37,38,39,40,41,42-hexolato)-

bis(dimethylsulfoxide)-tetrascandium(III) acetonedimethylsulfoxide solvate.

hydroxo)-bis(acetonitrile)-tetra-scandium(III) acetonitrile solvate.

10: bis(μ-5,11,17,23,29,35-hexa-*tert*-butylcalix[6]arene-37,38,39,40,41,42-hexolato)-bis(μ-oxo)-tetra-titanium unknown solvate)

12: bis(µ-benzoato)-(µ-5,11,17,23,29,35-hexa-tert-

 $butylcalix[6] are ne-37, 38, 39, 40, 41, 42-hexolato)-tetrakis(\mu-ethoxo)-bis(ethanol)-tetraethoxy-tetra-titanium ethanol unknown solvate)$

13: tetrakis(μ-benzoato)-(μ-5,11,17,23,29,35-hexa*tert*butylcalix[6]arene-37,38,39,40,41,42-hexolato)-bis(μisopropoxo)-bis(μ-oxo)-octakis(isopropoxy)-hexa-titanium unknown

solvate) **14**: bis(μ-5,11,17,23,29,35-hexa-*tert*butylcalix[6]arene-

*tert*butylheptacyclo[31.3.1.1₃,7.1_{9,13}.1_{15,19}.1_{21,25}.1_{27,31}]dotetraconta-1(37),3(42),4,6,9(41),10,12,15(40),16,18,21(39),22,24,27(38),28,30, 33,35-octadecaene-37,38,39,40,41,42-hexolato)-bis(μ-oxido)-

bis(*N*,*N*-dimethylformamide)-tetra-titanium(IV) propan-2-ol solvate).

16·*i*PrOH:octakis(μ-phenylphosphonato)-tetrakis(μ-hydroxido)-tetrakis(μ-trihydrogen5,11,17,23,29,35-hexatert-

butylheptacyclo[31.3.1.1_{3,7}.1_{9,13}.1_{15,19}.1_{21,25}.1_{27,31}]dotetraconta-1(37),3(42),4,6,9(41),10,12,15(40),16,18,21(39),22,24,27(38),28,30, 33,35-octadecaene-37,38,39,40,41,42-hexolato)-octa-titanium(IV) *N*,*N*-dimethylformamide propan-2-ol solvate.

1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-25,26,27,28-tetrolato) hexakis(μ -propan-2-olato)-tris(μ -oxide)-hexa-titanium(IV) dichloromethane solvate

18·MeCN: bis(μ -5,11,17,23,29,35-hexa-*tert*-butylcalixarene[6]-37,38,39,40,41,42-hexolato)-bis(acetonitrile)-tetra-titanium acetonitrile unknown solvate

19·4MeCN: (μ-5,11,17,23,29,35-

hexa-*tert*-butylcalix[6]arenel-37,38,39,40,41,42-hexolato)hexatriacontakis(μ -oxo)-tetratriacontakis(μ -propionato)bis(isopropanol)-octacosa-titanium acetonitrile unknown solvate) **20**·3.5 MeCN: μ -5,11,19,25,31,39-

hexa-*tert*-butyl-15,35-

dioxaheptacyclo[35.3.1.1₃,7.1₉,1₃.1₁₇,2₁.1₂₃,2₇.1₂₉,3₃]hexatetraconta-1(41),3(46),4,6,9(45),10,12,17(44),18,20,23(43),24,26,29(42),30,32, 37,39-octadecaene-41,42,43,44,45,46-hexolato]-(acetonitrile)diisopropoxy-di-titanium acetonitrile solvate)

21·MeCN: bis(µ-5,11,19,25,31,39-hexa-*tert*-butyl-15,35-

dioxaheptacyclo[35.3.1.1₃,7.1₉,1₃,1₁₇,21.1₂₃,27.1₂₉,3₃]hexatetraconta-1(41),3(46),4,6,9(45),10,12,17(44),18,20,23(43),24,26,29(42),30,32, 37,39-octadecaene-41,42,43,44,45,46-hexolato)-bis(μ -oxo)-aquatetra-titanium acetonitrile solvate)

22·2.5MeCN: hexakis(µ-fluoro)-(µ- dihydrogen-41,42,43,44,45,46-hexaoxy-5,11,15,19,25,31,35,39-octamethyl-

 $15,35, diazahepta cyclo [35.3.1.1_{3,7}.1_{9,13}.1_{17,21}.1_{23,27}.1_{29,33}] hexatetra contra-$

1(41),3(46),4,6,9(45),10,12,17(44),18,20,23(43),24,26,29(42),30,32, 37,39-octadecaene-15,35-di-ium)-octafluoro-tetra-titanium acetonitrile solvate)

23·5MeCN: {μ-dihydrogen-41,42,43,44,45,46-hexaoxy-5,11,15,19,25,31,35,39-octamethyl-15,35,-

diazaheptacyclo[35.3.1.1_{3.7}.1_{9,13}.1_{17,21}.1_{23,27}.1_{29,33}]hexatetraconta-1(41),3(46),4,6,9(45),10,12,17(44),18,20,23(43),24,26,29(42),30,323 7,39-octadecaene-15,35-di-ium)-(μ -oxo)-

diaquatetrachlorotetrachloro-di-titanium acetonitrile solvate.

25·7MeCN: (μ-41,42,43,44,45,46-hexaoxy-5,11,15,19,25,31,35,39octamethyl-15,35-

diazaheptacyclo[35,3,13,7,19,13,1,117,21,123,27,129,33]hexatetraconta-

1(41),3(46),4,6,9(45),10,12,17(44),18,20,23(43),24,26,29(42),30,32, 37,39-octadecaene-15,35-di-ium)-hexakis(acetonitrile)-

dodecabromo-tetra-titanium acetonitrile solvate.

26·2MeCN: *tert*-butylammonium (µ3-5,11,17,23,29,5-hexa*tert*butyl-37,38,39,40,41,42-hexaoxycalix[6]arene)-bis(µ2-oxo)-(*tert*butylimido)-(*tert*-butanol)-dioxo-tri-vanadium acetonitrile solvate)

28·8MeCN: tetrakis(acetonitrile)-lithium bis(μ -5,11,17,23,29,35-hexa-*tert*butyl-37,38-dihydroxy-39,40,41,42-

tetraoxidocalix[6]arene)-bis(μ -oxido)-(acetonitrile)-lithium(I)-divanadium(V) acetonitrile solvate)

29·2MeCN: catena-[bis(μ_3 -oxido)-(μ_2 -5,11,17,23,29,35-hexa-*tert*-butyl-37,40-dihydroxy-38,39,41,42-tetraoxidocalix[6]arene)-dioxo-

30·2Et₂O·0.5THF: (µ-5,11,17,23,29,35-hexa-*tert*butylheptacyclo[31.3.1.1_{3,7}.1_{9,13}.1_{15,19}.1_{21,25}.1_{27,31}]dotetraconta-1(37),3(42), 4,6,9(41), 10,12,15(40),16,18,21(39),22,24,27(38),28,30,33,35-octadecaene-37,38,39,40,41,42-hexalato)-tetrakis(µ-oxo)-

(diethylether)oxobis(tetrahydrofuran)-lithium-tri-vanadium diethylether-tetrahydrofuran solvate)).

 $\label{eq:32-5} \begin{array}{l} \textbf{32-5} MeCN: (\mu-5,11,7,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexaoxyhomodioxacalix[6]arene)-(\mu-oxo)-tetrakis(acetonitrile)-disodium-di-vanadium acetonitrile solvate) \end{array}$

33·6MeCN: (µ-5,11,7,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexaoxyhomodioxacalix[6]arene)-bis(µ-oxo)-bis(propan-1-olato)-tetraoxo-tetra-vanadium acetonitrile solvate).

34·4MeCN·CH₂Cl₂: (μ-5,11,7,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexaoxyhomodioxacalix[6]arene)-bis(4methylaniline)-di-vanadium acetonitrile dichloromethane solvate

 $\label{eq:states} \begin{array}{l} \textbf{35} \cdot \textbf{4MeCN:} \ (\mu-5,11,7,23,29,35-hexa-\textit{tert-butyl-}37,38,39,40,41,42-hexaoxyhomodioxacalix[6]arene)-bis((4-methoxyphenyl)imido)-divanadium(V) acetonitrile solvate \end{array}$

36: (μ-5,11,7,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexaoxyhomodioxacalix[6]arene)-bis((4-trifluoromethylphenylimido)-di-vanadium(V)

 $\begin{array}{l} \textbf{37:} (\mu\text{-}5,11,7,23,29,35\text{-}hexa\text{-}tert\text{-}butyl\text{-}37,38,39,40,41,42\text{-}hexaoxyhomodioxacalix[6]arene)\text{-}bis[(4\text{-}chlorophenyl)imido]divanadium \end{array}$

 $\label{eq:40} \begin{array}{l} \textbf{40} \cdot 2 \text{MeCN: } (\mu_2 \text{-} 5, 11, 17, 23, 29, 35 \text{-} hexa-\textit{tert-butyl-} 37, 38, 39, 40, 41, 42 \text{-} hexaoxycalix[6]arene)-bis(acetonitrile)-tetrachloro-di-niobium(V) acetonitrile solvate). \end{array}$

42·2MeCN: μ_2 -5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexaoxycalix[6]arene)-bis(acetonitrile)-tetrachloro-di-tantalum(V) acetonitrile solvate

43·4MeCN: Bis(μ₃-hydroxo)-bis(μ₃-η₆-5,11,17,23,29,35-hexa-*tert*-butyl-37,38,41-trihydroxycalix[6]arene-39,40,42-triolato)-

tetrakis(acetonitrile)-dichromium(III)-di-sodium acetonitrile solvate **44**·4MeCN: (2-(2-((1-

iminoethyl)amino)phenyl)ethyl)phenylimido-N,N')-

(5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40-tetraoxy-41,42dihydroxycalix[6]arene-O,O',O'',O''')molybdenum(VI) acetonitrile solvate)

47: (μ₂-5,11,17,23,29,35-hexa-*tert*-butylcalix[6]arene-37,38,39,40,41,42-hexaolato)-(μ₂-oxo)-bis(ethane-1,2-diolato) ditungsten **48**·2MeCN: (µ₂-5,11,17,23,29,35-hexa-*tert*butylcalix[6]arene-37,38,39,40,41,42-hexolato)-tetrakis(ethane-1,2-diolato)-ditungsten acetonitrile solvate)

49·0.83toluene·MeCN: (μ₂-5,11,19,25,31,39-hexa-*tert*-butyl-15,35dioxaheptacyclo[35.3..1.1_{3,7}.1_{9,13}.1_{17,21}.1_{23,27}.1_{29,33}]hexatetraconta-1(41),3(46),4,6,9(45),10,12,17(44),18,20,23(43),24,26,29(42),30,32, 37,39-octadecaene-41,42,43,44,45,46-hexolato) bis(ethane-1,2diolato)-dioxo-di-tungsten acetonitrile toluene solvate) **50**·9.46MeCN: bis(pentakis(acetonitrile)-sodium bis(μ₅-

5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-

$$\label{eq:constraint} \begin{split} hexaoxycalix[6]arene)-bis(\mu 4-oxo)-hexakis(acetonitrile)-diaquatetrairon(III)-tetra-sodium bis(\mu 4-5,11,17,23,23,29-hexa-tert-butyl-37,38,39,40,41,42-hexaoxycalix[6]arene)-bis(\mu 4-oxo)- \end{split}$$

bis(acetonitrile)-diaqua-tetra-iron(III)-di-sodium acetonitrile solvate) **52**·6MeCN: catena-((μ s-5,11,17,23,29,35-hexa*tert*-butyl-37,38,39,40,41,42-hexaoxycalix[6]arene)-(μ 4-oxo)-bis(μ 3-oxo)-(μ 2-

oxo)-(µ2-acetonitrile)-aqua-heptakis)acetonitrile)-

tetrairon(III)dipotassium acetonitrile solvate)

53·4MeCN/**54**·2MeCN: (μ₄-7,13,19,27,33,39-hexa*tert*-butyl-41,42,43,44,45,46-hexaoxy-2,3,22,23-tetrahomo-

3,23,dioxacalix[6]arene)-(µ2-oxo)-tetrakis(acetonitrile)-di-iron(III)di-sodium/potassium acetonitrile solvate)

57·3DMF: catena-(tris(*N*,*N*-dimethylformamide)-(μ₂-5,11,17,23,29,35-hexa-*tert*-butyl-37,40-dioxy-38,39,41,42tetrahydroxycalix[4]arene)-cobalt(II) *N*,*N*-dimethylformamide solvate).

58· $2H_2O$: Aqua-bis(*N*,*N*-dimethylformamide)-(7,13,19,27,33,39-hexa*tert*-butyl-41,43-dioxy-42,44,45.46-tetrahydroxy-2,3,22,23-tetrahomo-3,23-dioxacalix[6]arene)-cobalt(II)

N,Ndimethylformamide solvate monohydrate.

Carl Redshaw was (now Emeritus) Chair of Inorganic Materials at the University of Hull prior to the closure of the chemistry department. He has been Visiting Professor at Northwest University (Xi'an, China), Sichuan Normal University (Chengdu, China), the Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences (Shanghai, China), the Institute of Chemistry (ICCAS), Chinese Academy of Sciences (Beijing, China) and the National Institute of Technology (Akashi, Japan). Carl utilizes coordination chemistry to tackle issues ranging from catalysis to cancer.



