Insights into the structures adopted by titanocalix[6 and 8]arenes and their use in the ring opening polymerization of cyclic esters

Orlando Santoro, a Mark R. J. Elsegood, a,b Elizabeth V. Bedwell,b Jake A. Pryce, b and Carl Redshaw* a

Interaction of p-tert-butylcalix[6]areneH4, L1H4, with [TiCl4] afforded the complex [Ti4Cl4(OH)12(MeCN)2(L1H4)]·4.5MeCN (1.4.5MeCN; 1.4.5MeCN), in which two pseudo octahedral titanium centres are bound to one calix[6]arene. A similar reaction but employing THF resulted in the THF ring-opened product [TiCl4(L1H4)]·(O(CH2)4Cl)][4MeCN (2-4MeCN), where L1H4 = p-tert-butylcalix[4]areneH4. Interaction of L1H4 with TiF6 (3 equiv.) led, after work-up, to the complex ([TiF6(L1H4)]·H2O)6.5MeCN (3-6.5MeCN). Treatment of p-tert-butylcalix[8]areneH6, L2H6, with [TiCl4] led to the isolation of the complex ([TiCl4(TiNCMe)2(L1H4)]·1.5MeCN (4-1.5MeCN). From a similar reaction, a co-crystallized complex [Ti6O24(MeCN)26(L2H4)]·[TiCl4(MeCN)(OH)](L2H4)·H2O·11MeCN (5-H2O·11MeCN) was isolated. Extension of the L1H4 chemistry to [TiBr4] afforded, depending on the stoichiometry, the complexes ([TiBr4(TiNCMe)2(L1H4)]·6MeCN (6-6MeCN) or [Ti(NCMe)3Br]·[Ti(O)Br2(NCMe)Me(L1H4)]·7.5MeCN (7-7.5MeCN), whilst use of [TiF6] afforded complexes containing Ca2+ and Na+, thought to originate from drying agents, namely [Ti5CaF2(OH)4Na2(MeCN)(L1H4)]·14MeCN (8-14MeCN), [Na(MeCN)][Ti5CaF2Na(MeCN)(L1H4)]·7MeCN (9-7MeCN), or [Na][Ti5F2Na(MeCN)(L1H4)][TiF2Na(MeCN)(L1H4)]·15(C6H6·H2O) (10-15MeCN). In the case of Ti6H6, the ladder (Ti6H6)[Ti6Cl3(NCMe)2(L1H4)]·7.25H2O·Cl2·17.25CH3Cl] was isolated. These complexes have been screened for their potential to act as catalysts in the ring opening polymerization (ROP) of ε-caprolactone (ε-CL), β-valerolactone (β-VL) and rac-lactide (r-LA), both in air and N2. For ε-CL and β-VL, moderate activity at 130 °C over 24 h was observed for 1, 9 and 11; for r-LA, only 1 exhibited reasonable activity. In the case of the co-polymerization of ε-CL with ε-CL, the complexes 1 and 11 afforded reasonable conversions and low molecular weight polymers, whilst 4, 6, and 9 were less effective. None of the complexes proved to be active in the co-polymerization of ε-CL and r-LA under the conditions employed herein.

Introduction

Frameworks capable of binding multiple metal centres are of interest in catalysis given the potential for beneficial cooperative effects. [1] Our interest in this area has been, and remains, focused mostly around the use of the family of polyphenolic macrocycles called calix[n]arenes. [2] For the n = 4 system, namely p-tert-butyldiacalix[4]areneH4 (L4H4), the tendency is to coordinate to only one metal centre via the four phenolic oxygens (the lower rim) and usually the macrocycle retains the cone conformation. [3] Of the larger calix[n]arenes, the n = 6 (L1H6) and 8 (L2H8) systems are attractive scaffolds given their availability; odd numbered calix[n]arenes are isolated in far lower yields. [4] However, the coordination chemistry of the larger calix[n]arenes remains relatively unexplored. [2, 5] In the case of titanium, reports date back to the 1980s. [6] In our coordination studies employing different metals (i.e. tungsten and vanadium), we have had limited success for n = 6, [7] whilst previous work for n = 8 has shown that it is possible, via controlling the reaction stoichiometry, to incorporate selectively two, three, or four metal centres (W) at the lower rim. [8] Furthermore, the systems incorporating vanadium have exhibited high catalytic activities in the area of α-olefin polymerization. [9] In the area of ring opening polymerization (ROP) of cyclic esters, reports using metallocalix[n]arenes are scant. In the case of tungstocalix[6 and 8]arenes, we observed how different sized calixarenene rings and their associated conformations can drastically affect the catalytic activity for the ROP of ε-caprolactone (ε-CL). [10] More recently, McIntosh et al. of reported preliminary studies on the use of the complex [Ti4(L2)(ON-Pr)6(THF)2] as a catalyst for the ROP of rac-lactide (r-LA) at 130 °C. [11] Other titanocalix[n]arene work in this area employs the de-tert-butylnated n = 4 system (1,3-di-propylcalix[4]arene), with well-behaved ROP of rac-lactide observed when employing either microwave radiation or heat; the former method was beneficial to the rate of polymerization at the expense of control. [12] A related system, possessing para-NO2 and tert-butyl groups at the upper-rim of the calix[4]arene was capable of the well-controlled ROP of L- and r-LA under solvent-free conditions. [13] Recently, we have tested the efficiency of known complexes of the type [TiCl4L2(O)2(OR)3] (R = Me, n-Pr and n-pentyl), the Cl-bridged...
compound \([\text{TiL}_3(O)(OR)]_2(\mu-\text{Cl})_2\) (R = n-decyl) and the monochloride complex \([\text{Ti(NCMe)}_2\text{ClL(O)}_3(\text{OMe})]\) in the ROP of several cyclic esters. \([14]\) Although all complexes were found to be efficient for ROP, the monochloride species proved to be the best performing of the series. It is noteworthy that all catalysts were shown to be active even under aerobic conditions, without any significant activity loss. Moreover, titanocalix[4]arene species were shown to be better performing than other Ti-based benchmark catalysts (including a Ti-diphenolate compound), suggesting a positive effect of the calix[4]arene ligand on the catalyst efficiency. These limited studies suggest there is the potential for accessing both controllable and highly active ROP catalysts based on titanocalix[\(n\)]arenes with \(n \geq 6\). Herein, we focus on titanocalix[6 and 8]arenes derived from interaction of the parent \(p\)-tert-butylcalix[6 and 8]arenes, namely \(n = 6\) (L\(^1\)H\(_6\)) and \(n = 8\) (L\(^1\)H\(_8\)) with the tetrahalides \([\text{TiX}_4]\) (X = Cl, Br, F, I). A number of intriguing molecular structures...
(see charts 1 and Figures S1-2, ESI) have been identified, and the complexes have been screened for their ability to act as catalysts in the ROP of ɛ-CL, δ-valerolactone (δ-VL), and r-LA as well as for the copolymerization of ɛ-CL with ɛ-VL, and ɛ-CL with r-LA. We have recently reviewed the use of titanium diphenolates and titanocalix[4]arenes for both α-olefin polymerization and the ROP of cyclic esters. [15]

Results and Discussion

Use of p-tert-butylcalix[6]areneH₆ 1H₄

In the case of 1H₄, where L¹ = p-tert-butylcalix[6]arene, interaction with two equivalents of [TiCl₄] afforded, after work-up (MeCN), the complex [Ti₂Cl₃(MeCN)₂(OH₂)(L¹H₄)] [Ti₂Cl₃(MeCN)₃(L¹H₄)]-4.5 MeCN (1·4.5 MeCN) as orange crystals on slow cooling to ambient temperature. In the IR spectrum, ν(CN) for both coordinated and free acetonitrile (2319/2308 and 2289 cm⁻¹, respectively) are observed. The molecular structure (CCDC No 1973136) of 1 is shown in Figure 1, with selected bond lengths and angles given in the caption. The asymmetry unit contains two similar but unique molecules. In each case, the two pseudo octahedral Ti(IV) ions are bound to six ligands, one chlorido, acetonitrile molecules and water molecule are facial. In each molecule; the phenolic hydrogens on O(2) and O(2A) are retained, whilst Ti(1) is bonded to two Cl⁻ ions and one water molecule, Ti(1A) is bonded to two Cl⁻ ions and one MeCN molecule, and this is the chemical difference between the two unique metal complexes; Ti(2) and Ti(2A) are both bonded to one Cl⁻ ion and two MeCN molecules. There are hydrogen bonds between O(2) — H(2)···O(6A) and O(2A) — H(2A)···O(6).

Figure 1. Two views of the molecular structure of [Ti₂Cl₃(MeCN)₁(ΟΗ₂)₁(ΟΗ)₁][Ti₂Cl₃(MeCN)₃(ΟΗ)₁]-4.5 MeCN (1·4.5 MeCN). Solvent of crystallisation, minor components of disordered atoms, and most H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–O(1) 1.775(5), Ti(1)–O(2) 2.077(5), Ti(1)–O(3) 1.797(5), Ti(1)–O(4) 2.173(6), Ti(1)–Cl(1) 2.320(3), Ti(1)–Cl(2) 2.325(3), Ti(1)–O(5) 1.763(5), Ti(2)–O(6) 1.917(5), Ti(2)–O(7) 1.815(5), Ti(2)–N(11) 2.244(6), Ti(2)–N(8) 2.300(7), Ti(1)–Cl(1) 2.358(2), Ti(1)–O(1)–C(1) 172.4(5), Ti(1)–O(2)–C(12) 118.4(4), Ti(2)–O(6)–C(22) 159.9(4), Ti(2)–O(7)–C(23) 165.5(5), Ti(2)–O(6)–C(24) 117.3(4), Ti(2)–O(7)–C(26) 161.3(5)

The retention of a phenolic hydrogen on L¹, allows for hydrogen bonding with an oxygen on the other molecule in the asymmetric unit, or the next pair along the chain. These pairs of molecules form infinite, H-bonded, zig-zag chains, in the b-direction (see Figure S3, ESI). The coordination of the metal to the calix[6]arene and the conformation adopted by the macrocycle are reminiscent of that observed for the group V complexes {[M(NCMe)Cl₂L¹] (M = Nb, Ta). [16] When THF was employed as solvent, the orange/red complex [Ti₂Cl₃(μ-O₂)(NMCMe)₆(ΟΗ₂)₆]·4MeCN (2·4MeCN) was isolated in low yield. Its molecular structure (CCDC 1973134) is shown in Figure S4 of the Supporting Information. The molecule lies on a centre of symmetry, and was refined as a 2-component twin (components 0.5431:0.4569(10)); component 2 rotated by 8.1802° around [-0.01 0.98 0.18] (reciprocal) or [0.20 0.92 0.33] (direct). The core of the complex can be described as two, singly vertex-vacant cubes, connected by a face, in which the Ti octahedra share edges. Both Ti(2) and Ti(2A) possess O(CH₃)₂Cl groups. The main core of 2 was found to be similar to that of Ti(NMMe)₆[(μ₄-O)₉(O₂)₉(TiCl₄(O₂)₉)]·2[TiCl₃(NMMe)L(O₂)O(On-Pr)]·11MeCN, a compound we have recently reported. [14] The formation of 2 is thought to involve the ring opening of the THF, which has been reported in the literature for a number of systems, particularly in the presence of Lewis acids and more recently in the reaction between boryl triflates and arylloxides. [17] The presence of a calix[4]arene rather than a calix[6]arene...
is thought to be due to the presence of a small amount of the n = 4 macrocycle in the batch of the precursor used. In the case of TiF$_4$ (3 equiv.), reaction with L$_2$H$_4$ afforded, following extraction into MeCN, the orange/red complex [(TiF)$_2$]µ-F-LH$_4$]·6.5MeCN (3:6.5MeCN). The molecular structure (CCDC 2009076) is shown in Figure 2, with selected bond lengths and angles given in the caption. The molecule lies on a centre of symmetry and so half is unique. Two distorted octahedral titanium centres are bound to each of the two L$^-$ macrocycles, the latter being linked by H-bonds. The central core can be described as two Ti$_2$F$_4$ diamonds, which bridge the calixarenes, whilst two fluoride ions bridge the two diamonds. The Ti-F bonds are somewhat longer than those found in the O,N bridge the two diamonds. The Ti-F bonds are somewhat longer

Some weak C–H···Cl intermolecular interactions parallel to $\sigma$ bind molecules into anti-parallel stacks (see ESI, Figure S6). In one preparation of 4, following work-up and crystallization from MeCN, the isolated crystals were identified as [Ti$_2$O$_2$Cl$_4$(MeCN)$_2$(L$^-$)]$_2$[(TiCl)$_2$(MeCN)$_2$(OH$_2$)$_2$(L$^-$)]$_2$[OH$_2$]$_2$·11MeCN (5:11MeCN; CCDC 1973135). The asymmetric unit of 5 contains 2 different molecules (Figure 4). In one molecule there is a ladder structure, like 4, made up of four Ti(IV) ions and phenolate oxygen ligands (from the L$^-$ ligand) and bridging oxygens, O(3), O(7), O(9), and O(10). The latter two are oxo dianions. Ti(1) and Ti(4) each carry 1 Cl$^-$ ion and one MeCN ligand; Ti(2) and Ti(3) each carry one Cl$^-$ ion. In the other molecule, three Ti(IV) ions are coordinated to a L$^-$ ligand via 6 phenolate oxygens (two per Ti); and oxygens O(17) and O(18) remain protonated. Ti(5) and Ti(6) are each coordinated to two Cl$^-$ ions and two MeCN ligands, and Ti(7) is coordinated to two Cl$^-$ ions, one MeCN ligand and one water molecule. There are two intramolecular H-bonds: O(18)···H–O(17) and O(17)···H–O(19), and a lone water molecule sits between the two titanium-calixarene molecules. The H atoms could not be located for this or the coordinated water molecule, but both appear to form reasonable H-bonds: O(19)···Cl(9) = 2.681 Å, O(19)···O(20) = 2.759 Å, and O(20)···Cl(11) = 3.525 Å. In terms of intermolecular interactions between molecules, the water molecule between the two different calix[8]arene complexes hydrogen bonds to the coordinated water molecule. The coordinated water molecule H-bonds to an acetoniitrile molecule of crystallization.
Figure 4. Molecular structures of the two Ti complexes co-crystallised in [Ti$_4$O$_2$Cl$_4$(MeCN)$_2$](OH$_2$)$_2$][OH$_2$]·11MeCN (5·11MeCN). Solvent of crystallization, minor components of disordered atoms, and most H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–O(1) 1.798(3), Ti(1)–O(2) 1.796(3), Ti(1)–O(9) 1.958(3), Ti(1)–Cl(1) 2.3109(17), Ti(1)–N(1) 2.269(5), Ti(2)–O(9) 1.944(3), Ti(2)–O(9) 1.769(3), Ti(2)–O(9) 1.995(3), Ti(2)–O(10) 1.896(3), Ti(2)–Cl(2) 2.133(3), Ti(5)–O(11) 1.780(3), Ti(5)–O(12) 1.769(3), Ti(5)–Cl(5) 2.3707(19), Ti(5)–Cl(6) 2.3317(17), Ti(5)–N(1A) 2.233(4), Ti(5)–N(2A) 2.195(4), Cl(1)–Ti(1)–O(2) 102.51(12), O(1)–Ti(1)–O(9) 107.79(14), Cl(1)–Ti(1)–N(1) 172.39(10), O(3)–Ti(2)–O(4) 95.74(13), Cl(2)–Ti(2)–O(3) 105.99(12), Cl(2)–Ti(2)–Cl(6) 162.91(7), O(11)–Ti(3)–N(1A) 88.65(15), O(12)–Ti(3)–N(1A) 88.58(16), Cl(7)–Ti(6)–O(13) 165.98(7), O(13)–Ti(6)–N(4A) 169.60(16), Cl(9)–Ti(7)–Cl(10) 167.29(6), O(15)–Ti(7)–N(5A) 173.91(15), H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–O(1) 1.8153(15), Ti(1)–O(2) 1.7834(16), Ti(1)–O(9) 1.8153(15), Ti(1)–Cl(1) 2.4484(5), Ti(1)– Cl(2) 2.327(2), Ti(2)–O(8) 1.9490(15), Ti(2)–O(7) 1.7620(15), Ti(2)–O(9) 1.9819(16), Ti(2)–O(10) 1.8859(15), Cl(1)–Ti(1)–Cl(2) 2.3871(4), Ti(1)–O(1)–C(1) 130.18(14), Ti(1)–O(2)–O(8) 136.69(16), Ti(1)–O(9)–Ti(3) 158.93(14), Ti(1)–O(9)–C(78) 126.59(12), Ti(2)–O(8)–C(67) 166.45(15), Ti(1)–O(9)–Ti(2) 103.12(6), Ti(1)–O(9)–Ti(3) 146.33(9), O(8)–Ti(2)–O(10) 146.05(7).

Figure 5. Two views of the molecular structure of [TiBr$_2$(TiBrNCMe)$_2$(μ-3-O)$_2$](L$_2$)$_2$]·6MeCN (6·6MeCN). MeCN of crystallization, minor components of disordered atoms, and H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–O(1) 1.8153(15), Ti(1)–O(2) 1.7834(16), Ti(1)–O(9) 1.9668(16), Ti(1)–Br(1) 2.4484(5), Ti(1)–N(1) 2.3871(4), Ti(2)–O(8) 1.9490(15), Ti(2)–O(7) 1.7620(15), Ti(2)–O(9) 1.9819(16), Ti(2)–O(10) 1.8859(15), Ti(2)–Br(2) 2.3871(4), Ti(1)–O(1)–C(1) 130.18(14), Ti(1)–O(2)–C(12) 158.93(14), Ti(1)–O(9)–C(78) 126.59(12), Ti(2)–O(8)–C(67) 166.45(15), Ti(1)–O(9)–Ti(2) 103.12(6), Ti(1)–O(9)–Ti(3) 146.33(9), O(8)–Ti(2)–O(10) 146.05(7).
Both coordinated MeCN groups point to the same side of the molecule, whilst the six MeCN molecules of crystallization are all exo to the complex. Molecules pack in layers. Adjacent molecules within layers adopt up-down-up-down orientations (see Figure S7, ESI). Between layers molecules stack in columns all pointing in the same direction with weak Br(1)...Br(2') = 3.770 Å halogen bonding interactions. Given the addition of differing amounts of metal chloride to a calix[n]arene can be used to control the degree of metatation, [8] we also investigated the addition of three equivalents of [TiBr₄]. This resulted, following work-up (MeCN), in the formation of brown prisms for which a molecular structure determination revealed the asymmetric unit ([TiBr₂H₂O)(NCMe)][TiBr₂(NCMe)₂Ti₂L₂H₄]·7.5(MeCN) [7-7.5(MeCN)], see Figure 6 (CCDC No. 1973131). The calix[8]arene ligand retains two phenolic hydrogens on oxygens O(7) and O(8), which are not bound to titanium ions. Three TiBr₂ moieties bind to the L₂H₄ via two phenolate oxygens each. Each Ti ion has octahedral geometry. The bromides are trans on Ti(1) and Ti(2), but cis on Ti(3).

![Figure 6. Molecular structure of [Ti(NCMe)Br₂][Ti(OBr₂(NCMe))[L²]]·7.5MeCN (7-7.5MeCN). Calixarene 8H groups, minor components of disordered atoms, and MeCN of crystallization omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)--O(1) 1.793(5), Ti(1)--O(2) 1.796(5), Ti(1)--O(9) 2.154(6), Ti(1)--Br(1) 2.5066(15), Ti(1)--Br(2) 2.5496(14), Ti(1)--N(1) 2.193(7), Ti(2)--O(3) 1.785(4), Ti(2)--O(4) 1.777(5), Ti(2)--Br(3) 2.5224(16), Ti(2)--Br(4) 2.5375(16), Ti(2)--N(3) 2.206(5), Ti(2)--N(4) 2.228(6), Ti(3)--O(5) 1.734(4), Ti(3)--O(6) 1.808(5), Ti(3)--Br(5) 2.4653(13), Ti(3)--Br(6) 2.5371(13), Ti(3)--N(5) 2.198(5), Ti(3)--N(6) 2.260(7), Ti(3)--O(9) 1.146(14), Ti(3)--O(2)--C(12) 150.3(4), br(1)--Ti(1)--Br(2) 166.29(7), O(1)--Ti(1)--O(9) 170.4(2), Ti(2)--O(3)--C(23) 151.1(4), Ti(2)--O(4)--C(34) 150.7(4), Br(3)--Ti(2)--Br(4) 169.37(6), Ti(3)--O(5)--C(45) 152.4(4), Ti(3)--O(6)--C(56) 155.5(4), Br(5)--Ti(3)--Br(6) 94.43(5).]

The remaining coordination sites are occupied by MeCN ligands in the case of Ti(2) and Ti(3), while Ti(1) bears one MeCN and most likely a water molecule. No peaks corresponding to carbon atoms were evident close to that water molecule that would have indicated MeCN. There is one intramolecular hydrogen bond between one of the phenol groups and one of the coordinated bromide ions. The other phenolic hydrogen does not make a hydrogen bond. Molecules are arranged in an undulating layer structure in the a/c plane (see Figure S8, ESI).

Use of [TiF₄]: Use of [TiF₄] and L₂H₄ led, following work-up in MeCN, to more complicated species in which both sodium and calcium have been incorporated. The presence of these alkali/alkaline earth metals is thought to arise from the pre-drying of the solvents, namely toluene and acetonitrile respectively. The small red prisms obtained were subjected to an X-ray diffraction study (CCDC No 1973130), and two views of the molecular structure of 8 are given in Figure 7 (an alternative view is given in the ESI, Figure S9); selected bond lengths and angles are given in the caption. The complex has the formula [Ti₈CaF₂₀(OH₂)Na₂(MeCN)₆(L²)₂]·14MeCN (8-14MeCN), and lies on a mirror plane, which includes atoms Ca(1), Na(1), Na(2), some of the fluoride ions and the water molecule. The main core of the molecule comprises 8 titanium ions and 20 fluoride ions (a mixture of terminal and bridging), see Figure 7. Each titanium ion binds to a L² ligand via two phenolate oxygens, and each L² binds to four octahedral titanium ions. The oxygens bound to each individual titanium atom are cis. A calcium ion and two sodium ions are present to balance out the overall charge. The part of the core of the molecule containing the Ca²⁺ ion is antifluorite-like with the Ca²⁺ coordinated by 9 F ions. Na(1) interacts with fluorides F(6) and F(6A), and three acetonitrile molecules: via N(1), N(1A), and N(2). Na(2) interacts with fluorides F(8) and F(8A), water molecule O(9), and three acetonitrile molecules: containing N(4), N(5), and N(5A). The H atoms on the water molecule could not be located from difference maps. The water molecule bridges the calcium ion and one of the sodium ions. Four of the calixarene rings of each separate calixarene, bound to O atoms O(3), O(3A), O(4), and O(4A) on one, and O(5), O(5A), O(6), and O(6A) on the other, are close in space and adopt the same conformation, stacking almost exactly on top of each other, see Figures 8 and S9, ESI. The titanocalix[8]arene molecules are generally well separated, with no significant intermolecular interactions between them. Viewed perpendicular to b/c plane, it can be seen that there are significant solvent filled voids in the structure (Platon Squeeze recovers 291 electrons in 2 voids, giving 14 MeCNs per unit cell or an extra 7 MeCNs per Ti₈ complex), see Figure S10, ESI. [21]
Figure 7. Two views of the molecular structure of [Ti₈CaF₂₀(OH)₂Na₂(MeCN)₄(L)₂]·14MeCN (8·14MeCN). MeCN of crystallization, calixarene tBu groups, minor components of disordered atoms, and H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–O(1) 1.757(7), Ti(1)–O(2) 1.790(6), Ti(1)–F(1) 1.903(7), Ti(1)–F(2) 1.957(6), Ti(1)–F(3) 2.009(4), Ti(1)–F(9) 2.012(5), Ti(2)–O(3) 1.775(4), Ti(2)–O(4) 1.760(6), Ti(2)–F(3) 1.938(4), Ti(2)–F(4) 1.907(4), Ti(2)–F(5) 2.020(4), Ti(2)–F(10) 2.0063(14), Ti(3)–O(5) 1.802(5), Ti(3)–F(5) 1.796(4), Ti(3)–F(16) 1.806(5), T(3)–F(3) 1.983(4), T(3)–F(11) 1.9688(15), T(4)–O(7) 1.797(4), T(4)–O(8) 1.782(6), T(4)–F(4) 2.036(5), T(4)–F(7) 1.956(4), T(4)–F(8) 1.839(4), T(4)–F(12) 2.0104(16), Ca(1)–F(1) 2.889(6), Ca(1)–F(5) 2.869(4), Ca(1)–F(8) 2.716(5), Ca(1)–F(9) 2.776(11), Ca(1)–F(10) 3.027(5), Ca(1)–F(12) 2.858(7), Ti(1)–F(9)–Ti(1A) 146.0(7), Ti(1)–F(3)–Ti(2) 168.1(2), Ti(2)–F(10)–Ti(2A) 160.7(3), Ti(2)–F(5)–Ti(4) 152.3(2), Na(2)–O(9)–Ca(1) 85.8(4).

Figure 8. Side view (left) and core of the structure (right) of [Ti₈CaF₂₀(OH)₂Na₂(MeCN)₄(L)₂]·14MeCN (8·14MeCN).

We note that Ti-F complexes in which alkaline or alkaline-earth metal ions are featured in the structure in a host-guest fashion have been previously reported. [22] However, these species were intentionally synthesized in a template-controlled manner, while the Na and Ca ions present in 8 are likely to derive from the drying agents of the solvents used for the reaction/workup and are serendipitously incorporated into the structure. To investigate the reproducibility of such species, we repeated the reaction (using the same batch of L²H₄) and again isolated red prisms. However, on this occasion the asymmetric unit (CCDC No. 1973365) was found to be [Na(MeCN)₄][Ti₈CaF₂₀NaO₁₆(L)₂]·7MeCN (9·7MeCN), see Figure
9, and unlike 8·14MeCN, it is not on a mirror plane, i.e. the whole atoms. Ti(1) and Ti(2) have 2 terminal and 2 bridging fluorides, molecule is unique, although there are also many similarities. The main core of the molecule again comprises 8 titanium ions and 20 fluoride ions with the fluorides a mixture of terminal and bridging Ti(3) and Ti(4) have 4 bridging fluorides, and Ti(5) > Ti(8) have 1 terminal and 3 bridging fluorides. Each octahedral titanium ion binds to an L\(^2\) ligand via two phenolate oxygens; each L\(^2\) binds to 4 titanium atoms. The oxygens bound to each individual titanium atom are cis. A calcium ion and two sodium ions are present to balance out the overall charge. The part of the core of the molecule containing the Ca\(^{2+}\) ion (see Figure 10) is antifluorite-like with the Ca\(^{2+}\) coordinated by 11 F\(^-\) ions, rather than the 9 in 8. Na(1) interacts with fluoride F(1), phenolate oxygen O(1), two ipso phenolate carbons C(1) and C(78), and the n-system of phenolate ring C(67) > C(72). Na(2) binds to two acetonitrile molecules, via N(1) and N(2), as a separate moiety in fairly close proximity to the Ca\(^{2+}\) ion and its coordinated fluorides.

![Figure 9](image_url)

Figure 9. Two almost perpendicular views of the molecular structure of [Na(MeCN)]\(_2\) [Ti\(_8\)F\(_{20}\)NaO\(_{21}\)(L\(_2\))]·7MeCN (9·7MeCN). MeCN of crystallization, calixarene tBu groups, minor components of disordered atoms, and H atoms omitted for clarity. Selected bond lengths (Å) and angles (\(^°\)): Ti(1)–O(1) 1.812(4), Ti(1)–O(2) 1.769(5), Ti(1)–F(1) 2.014(5), Ti(1)–F(2) 1.895(4), Ti(1)–F(3) 2.013(3), Ti(1)–F(4) 2.028(4), Ti(2)–O(4) 1.831(4), Ti(2)–F(1) 2.033(3), Ti(2)–F(5) 1.938(4), Ti(2)–F(6) 1.892(4), Ti(2)–F(7) 2.033(4), Ti(3)–O(5) 1.778(4), Ti(3)–O(6) 1.763(4), Ti(3)–F(7) 1.961(4), Ti(3)–F(8) 2.002(3), Ti(3)–F(9) 1.927(3), Ti(3)–F(10) 2.003(3), Ti(4)–O(7) 1.791(5), Ti(4)–O(8) 1.779(4), Ti(4)–F(4) 1.949(4), Ti(4)–F(8) 2.002(3), Ti(4)–F(11) 1.919(4), Ti(4)–F(12) 2.038(4), Ti(5)–O(9) 1.788(4), Ti(5)–O(10) 1.807(5), Ti(5)–F(11) 2.021(4), Ti(5)–F(13) 1.829(4), Ti(5)–F(14) 1.963(3), Ti(5)–F(15) 2.009(4), Ti(6)–O(11) 1.793(5), Ti(6)–O(12) 1.786(4), Ti(6)–O(19) 2.027(3), Ti(6)–F(14) 1.973(3), Ti(6)–F(16) 1.829(4), Ti(6)–F(17) 1.961(4), Ti(6)–F(18) 1.894(4), Ti(6)–F(19) 2.054(3), Ti(8)–O(15) 1.795(5), Ti(8)–O(16) 1.838(4), Ti(8)–F(12) 2.051(4), Ti(8)–F(15) 1.950(4), Ti(8)–F(19) 2.025(3), Ti(8)–F(20) 1.857(4), Ca(1)–F(2) 2.736(4), Ca(1)–F(3) 2.669(4), Ca(1)–F(6) 2.888(4), Ca(1)–F(7) 3.073(4), Ca(1)–F(8) 3.068(4), Ca(1)–F(10) 2.807(3), Ca(1)–F(12) 2.901(4), Ca(1)–F(18) 2.675(4), Ca(1)–F(19) 2.809(4), Ca(1)–F(20) 2.773(4), Ti(1)–F(3)–Ti(2) 152.3(2), Ti(1)–F(4)–Ti(4) 162.68(19), Ti(2)–F(7)–Ti(3) 167.34(18), Ti(3)–F(8)–Ti(4) 159.17(19), F(2)–Ca(1)–F(10) 153.10(13), F(3)–Ca(1)–F(9) 150.59(13).

Again, as in 8, four of the calixarene rings of each separate calixarene, bound to O atoms O(5) > O(8) on one, and O(9) > O(12) on the other, are close in space and adopt the same conformation, stacking almost exactly on top of each other. MeCN molecules and MeCN-solvated Na\(^{+}\) ions lie between titanocalix[8]arene complexes. The complex [Na\(_2\)]\(_4\) [Ti\(_8\)F\(_{20}\)NaO\(_{21}\)(L\(_2\))]·7MeCN (10·7.5MeCN) has also been isolated and structurally characterized (see Figure 11) from a re-run of this type of reaction, indicating that the products formed are variable and their exact nature is determined by the presence of drying agents in the solvents. For 10, there are negative charges: 2 × calix[8] = 16–, 20 × F\(^-\) = 20–, total 36–; positive charges: 8 × Ti\(^{4+}\) = 32+, and 1 × Na\(^{+}\) gives a total of 33+. It is assumed that there are also another 3 Na\(^{+}\) ions to balance the charge and these are modelled by the Platon Squeeze procedure due to disorder and being randomly distributed between the MeCN molecules of crystallization. [21] The amount of MeCN of crystallization should be regarded as approximate. There are two almost identical molecules in the asymmetric unit, differing only in the coordination site of the sodium ion and the number of acetonitrile molecules bonded to the sodium. The main core of each molecule is made up of 8 titanium ions and 20 fluorides as seen previously in 8 and 9 (see Figure 12, and Figure S11, ESI). Two titanium ions have 2 terminal fluorides and 2 bridging fluorides, four titanium ions have 1 terminal fluoride and 3 bridging fluorides, and the remaining two titanium ions have 4 bridging fluorides. Each titanium ion binds to a L\(^2\) ligand via two phenolate oxygens; and each L\(^2\) binds to 4 titanium ions. Each Ti ion has octahedral geometry. The oxygens bound to each individual titanium atom are cis. In the first molecule, sodium ion Na(1) interacts with fluoride F(6) and two acetonitrile molecules including N(5) and N(9). In the second molecule, the major occupancy site of disordered sodium ion Na(2) interacts with fluorides F(25) and F(28), and the acetonitrile molecule including N(11), which was refined at half occupancy to match that of the major Na(2) component. Each pair of calixarene rings, on each titanium-fluoride core, are close in space and adopt the same conformation, stacking almost exactly on top of each other as...
seen previously (see Figures 12 and S12, ESI). MeCN molecules lie between titanocalixarene complexes. Also in this case, the Ti-F bonds for complexes 8-10 are slightly longer than those observed in previously reported compounds. [18]

**Figure 10.** Core of the structure of \([\text{Na(MeCN)}_2][\text{Ti}_8\text{CaF}_{20}\text{NaO}_{16}(L^2)_2]\cdot7\text{MeCN}\) (9·7MeCN).

**Figure 11.** The molecular structure of \([\text{Na}_6[\text{Ti}_8\text{F}_{20}\text{Na}(\text{MeCN})_2(L^2)]^{-}[\text{Ti}_8\text{F}_{20}\text{Na}(\text{MeCN})_0.5(L^2)]^{-}15.5\text{C}_2\text{H}_3\text{N}\) (10·15.5MeCN). Calixarene 'Bu groups, minor components of disordered atoms, MeCN of crystallization, and H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–F(1) 1.905(4), Ti(1)–F(2) 2.079(4), Ti(1)–F(9) 1.991(3), Ti(1)–F(12) 1.980(3), Ti(2)–F(9) 1.924(3), Ti(3)–F(10) 1.994(3), Ti(3)–F(11) 1.950(3), Ti(3)–F(6) 2.020(4), Na(1)–F(6) 2.696(4), Ti(1)–F(9)–Ti(2) 157.05(18), Ti(1)–F(12)–Ti(4) 149.4(2), Ti(3)–F(10)–Ti(12) 160.26(17), Ti(3)–F(11)–Ti(4) 165.40(17), Ti(5)–F(20)–Ti(8) 160.75(18).

**Figure 12.** Diagram of 10, emphasizing the core connectivity and partial calixarene overlay. Calixarene 'Bu groups, MeCN of crystallization, and H atoms omitted for clarity.

**Use of \([\text{TiI}_4]\):** Treatment of \(L^2\text{H}_8\) with four equivalents of \([\text{TiI}_4]\) in toluene afforded, following work-up in dichloromethane, a dark red complex which was isolated as large blocks. Interestingly, the molecular structure revealed (see Figure 12) a ladder complex similar to that observed for the chloride and bromide systems. The asymmetric unit comprises \([\text{TiI}_4\text{O}_2(\text{MeCN})_2(L^2)]^{-}7.25(\text{CH}_2\text{Cl}_2)\) (11·7.25CH₂Cl₂; CCDC 1973364). There are CH₂Cl₂ molecules both in calixarene clefts and exo to the calix[8]arene. There are some C–H···π interactions involving CH₂Cl₂ to calixarene rings. The molecules form layers in the a/c plane (see Figure S13, ESI).

Table 1 summarises the Ti–X bond length data from the four ladder structures described above. There are two main observations. Firstly, the Ti–X bond length increases by approx. 0.2 Å on going from Cl to Br and from Br to I, in line with the ionic radius increases as Group 17 is descended. Secondly, the Ti–X bond lengths for the halide attached to the six-coordinate end Ti ions, and trans to an MeCN nitrogen, is significantly longer (by 0.07 – 0.12 Å) than those for the apical halide attached to the central, five-coordinate, Ti ions with approx. square-based pyramidal geometry.

**Figure 13.** Molecular structure of \([\text{Ti}_4\text{I}_4\text{O}_2(\text{MeCN})_2(L^2)]^{-}7.25(\text{CH}_2\text{Cl}_2)\) (11·7.25CH₂Cl₂). CH₂Cl₂ of crystallization, minor components of disordered atoms, and H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–O(1) 1.792(7), Ti(1)–O(2) 1.792(7), Ti(1)–F(1) 1.905(4), Ti(1)–F(2) 2.079(4), Ti(1)–F(9) 1.991(3), Ti(1)–F(12) 1.980(3), Ti(2)–F(9) 1.924(3), Ti(3)–F(10) 1.994(3), Ti(3)–F(11) 1.950(3), Ti(3)–F(6) 2.020(4), Na(1)–F(6) 2.696(4), Ti(1)–F(9)–Ti(2) 157.05(18), Ti(1)–F(12)–Ti(4) 149.4(2), Ti(3)–F(10)–Ti(12) 160.26(17), Ti(3)–F(11)–Ti(4) 165.40(17), Ti(5)–F(20)–Ti(8) 160.75(18).
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1.825(6), Ti(1)–O(3) 2.165(6), Ti(1)–O(9) 1.959(7), Ti(1)–N(1) 2.676(2), Ti(1)–N(1)
2.274(11), Ti(2)–O(3) 1.940(6), Ti(2)–O(4) 1.754(6), Ti(2)–O(9) 2.009(7), Ti(2)–O(10)
1.898(6), Ti(2)–I(2) 2.5933(18), O(1)–Ti(1)–O(2) 100.5(2), O(1)–Ti(1)–O(9) 106.7(3), O(1)–
Ti(1)–N(1) 173.7(2), O(3)–Ti(2)–O(4) 96.6(3), O(2)–Ti(2)–O(3) 108.1(2).

Table 1. Summary of Ti–X bond lengths in [BuCalix[8]arene ladder structures.

| Structure | X | Av. Ti–X for X on central Ti (Å) | Av. Ti–X for X on end Ti (Å) | Difference, Δ (Å) |
|-----------|---|---------------------------------|-----------------------------|------------------|
| 4 & 5     | Cl| 2.173(2)                        | 2.297(2)                    | 0.124            |
| 6         | Br| 2.381(4)                        | 2.448(6)                    | 0.067            |
| 11        | I | 2.592(2)                        | 2.682(2)                    | 0.090            |

For catalysis comparison purposes, we have synthesised two diphenolate complexes bearing Br and I labile ligands, namely 12 and 13 (Scheme 1).

Scheme 1. Synthesis of the diphenolate complexes 12 and 13. [14]

For the bromo-derivative 12, crystals suitable for X-ray analysis were obtained at room temperature from a saturated solution of the compound in hexane. The molecular structure of the complex (CCDC 2009076) is shown in Figure 14. The compound features a tetrahedral Ti⁴⁺ ion. The complex molecule and the hexane of crystallization both lie on a mirror plane, so half of the formula is unique. The dihedral angle between aromatic rings was found to be 64°. The hexane molecule lies in the cleft between the two aromatic rings. There is a weak C–H···Br interaction between the methyl group at C(16) and Br(1) with an H(16A)···Br(1) distance of 3.05 Å.

Figure 14. Molecular structure of [TiBr₂(diphenolate)]·hexane (12·hexane). Most H atoms and minor components of disordered atoms omitted for clarity. Selected bond lengths (Å) and angles (º): Ti(1)–O(1) 1.7597(18), Ti(1)–Br(1) 2.3796(7), Ti(1)–
Br(2) 2.3810(7), O(1)–Ti(1)–Br(1) 110.55(6), Br(1)–Ti(1)–Br(2) 109.14(3), O(1)–
Ti(1)–O(1A) 104.85(12), O(1A)–Ti(1)–Br(1) 110.85(7). Symmetry operator A = 

ROP screening

ε-Caprolactone (ε-CL)

We have examined the ability of the complexes prepared herein to act as catalysts for the ROP of ε-CL (Table 2). At 80 °C, 1, 4 and 6 were found to be inactive (runs 1, 7, and 10). By increasing the temperature to 130 °C, 69% conversion was achieved in the presence of 1 in 24 h, while low activity was observed after 1 h (runs 3 and 5). Interestingly, the complex proved to be active also under aerobic conditions achieving ca. 20% conversion during 24 h (run 4). The Mₙ of the isolated polymers were found to be lower than the calculated values, while narrow polydispersities (1.20) were observed. Complex 3 was found to be inactive (run 6). Amongst the larger titanocalix[8]arene complexes, moderate conversion of the monomer was achieved only in the presence of 9 and with its iodo-congener 11 (63 and 74%, runs 13 and 15 respectively), while both chloro- and bromo-derivatives were found to be inactive. The higher activity of 1 compared with that of 4 and 6 can be explained considering the lability of the ligands present. In fact, the Ti ions in 1 are bound either to MeCN or H₂O, which are more readily lost than the halides in 4 and 6. Similarly, the lability of the iodo-ligands would be responsible for the higher activity of 11 compared to that of its Cl- and Br-containing analogues. This is in line with our recent study on titanocalix[4]arenes, in which the presence of a labile ligand (i.e. MeCN) proved beneficial for the catalyst activity. [14] In addition, the arrangement of and distance between the two Ti centers in 1 could favour cooperative effects enhancing the catalytic performances. On the other hand, this might not be possible for 4, 6, and 11 in which the metals are connected in a [Ti–O–Ti] fashion. Similar trends were observed in the case of multimetallic Al complexes bearing macrocyclic Schiff-bases, where both the distance and bond types present dictated the observed activity. [23] The efficiency of 9 is thought to be due to cooperative effects of the Ti and of Ca/Na cations present in the structure.

10 | J. Name., 2012, 00, 1-3 | This journal is © The Royal Society of Chemistry 20xx
Table 2. ROP of ε-CL using complexes 1, 3, 4, 6, 9 and 11-13.

| Run | Catalyst | e-CL:Ti:BnOH | T (°C) | Time (h) | Conv.a (%) | M_n calcd.d | M_w/M_n b |
|-----|----------|--------------|-------|----------|------------|-------------|-------------|
| 1   | 1        | 500:1:3      | 80    | 24       | none       | -           | -           |
| 2   | 1        | 250:1:3      | 130   | 24       | 69         | 5,240       | 6,700       |
| 3   | 1        | 250:1:3      | 130   | 1        | 6.5        | -           | -           |
| 4   | 3        | 500:1:3      | 130   | 24       | 20         | 2,690       | 3,860       |
| 5   | 3        | 500:1:3      | 130   | 1        | none       | -           | -           |
| 6   | 3        | 250:1:4      | 130   | 24       | none       | -           | -           |
| 7   | 4        | 500:1:2      | 80    | 24       | none       | -           | -           |
| 8   | 4        | 250:1:1      | 130   | 24       | 8.4        | -           | -           |
| 9   | 4        | 250:1:1      | 130   | 1        | none       | -           | -           |
| 10  | 6        | 500:1:2      | 80    | 24       | none       | -           | -           |
| 11  | 6        | 250:1:1      | 130   | 24       | none       | -           | -           |
| 12  | 6        | 250:1:1      | 130   | 1        | none       | -           | -           |
| 13  | 9        | 250:1:1      | 130   | 24       | 64         | 8,590       | 18,230      |
| 14  | 9        | 250:1:1      | 130   | 1        | none       | -           | -           |
| 15  | 11       | 250:1:1      | 130   | 24       | 74         | 6,610       | 21,110      |
| 16  | 11       | 250:1:1      | 130   | 1        | none       | -           | -           |
| 17  | 12       | 250:1:2      | 80    | 24       | >99        | 6,720       | 14,210      |
| 18  | 12       | 250:1:2      | 130   | 24       | >99        | 5,790       | 14,210      |
| 19  | 13       | 250:1:2      | 80    | 24       | 42         | liquid oligomers | -           |
| 20  | 13       | 250:1:2      | 130   | 24       | >99        | 5,640       | 14,210      |

a) Determined by 1H NMR spectroscopy on crude reaction mixture. b) From GPC. c) Values corrected considering Mark-Houwink factor (0.56) from polystyrene standards in THF. d) Calculated from [(Monomer]/[OH]) × conv. (%) × Monomer molecular weight + Molecular weight of BnOH. e) Reaction performed in air.

The bromo- (12) and iodo- (13) diphenolate titanium complexes were next investigated. Full conversion was achieved in the presence of the bromo derivative 12 at 80 °C within 24 h (run 17) affording a polymer with $M_n$ of ca. 6.7 kDa and rather narrow polydispersity (1.40). Interestingly, complex 12 proved to be efficient also under aerobic conditions at 130 °C, but with less control (run 18). However, in both cases, the $M_n$ were found to be much lower than the calculated values, suggesting the occurrence of transesterification processes. 1H NMR spectroscopic analysis on the sample isolated in run 16 highlighted the presence of signals at 7.33, 5.09 and 3.64 ppm in an integration ratio of 5:2:2, compatible with the presence of both BnO- and CH$_2$OH end groups (Figure S14, ESI). This was further confirmed by mass spectrometry. Indeed, the MALDI-ToF spectrum of the sample displayed a major series of peaks separated by 114 m/z units attributable to α-BnO-ω-OH terminated PCL n-mers as well as a minor population attributed to the corresponding Na$^+$ adducts (Figure S15, ESI). The iodocongener 13 was shown to be less efficient, affording 40% conversion at 80 °C (run 19) and low molecular weight oligomers. Interestingly, full conversion was achieved on increasing the temperature to 130 °C, affording a polymer of $M_n$ 5.6 kDa with good control ($M_w/M_n$ 1.30) (run 20). The higher activity of the diphenolate complexes can be ascribed to the increased accessibility of their metal centres compared to that of the calix[n]arene derivatives. However, 12 and 13 proved less active than related diphenolate species previously reported by Aida et al. [24]

δ-Valerolactone (δ-VL)

Furthermore, the ROP of δ-valerolactone (δ-VL) was investigated (Table 3). Similar to the previous case, 1 was found to be poorly active at 80 °C (runs 1 and 2). By increasing the temperature to 130 °C and lowering the monomer to catalyst ratio, moderate conversion was achieved in 24 h (run 3). For the isolated polymer, narrow polydispersity (1.13) and $M_n$ higher than the calculated value were observed. No conversion was achieved by preforming the reaction in air (run 4). Also in this case, 3 and 4 were found to be inactive (runs 5-9) while poor activity was exhibited by its Br-congener (runs 10-13). Moderate activity was exhibited by 9 over 24 h, affording a polymer of $M_n$ close to the calculated values and with good selectivity (run 14). No reaction was observed after 1 h (run 15). Interestingly, ca. 70% conversion was obtained in the presence of 11 over 24 h (run 16). The $M_n$ value was higher than the expected value and good control was observed. In the case of
the di-phenolate derivatives 12 and 13, at 80 °C within 24 h, only 52 and 41% conversion was achieved in the presence of the Br- and I-complexes, respectively (runs 18 and 20). The improvement of the conversion was observed on increasing the temperature to 130 °C (runs 19 and 21). In fact, 64 and 53% conversion was achieved with 12 and 13, respectively.

In both cases, polymers with $M_n$ lower than the calculated values were isolated; however, better control was exhibited by 13 compared with its bromo-congener ($M_n/M_w$ 1.4 vs 1.9).

rac-Lactide (r-LA)

All complexes were also employed as catalysts in the ROP of r-LA (Table 4). Good conversion was achieved in the presence of 1 (87%, run 1). The $M_n$ of the polymer was lower than the calculated value albeit with narrow molecular weight distribution (8,000 and 1.29, respectively). The syndiotactic bias ($P_s$) was determined by 2D J-resolved NMR spectroscopy (See Figure S16, ESI). [25] The observed value (0.51) suggested the formation of atactic PL. No reaction was observed when employing 3, 4, and the bromide complex 6, regardless of the reaction conditions investigated (runs 3-11). Unlike the previous cases, 9 was found to be completely inactive (runs 12 and 13). Eventually, 8% conversion was obtained in the presence of 11 over 24 h (run 14). On conducting the reaction in the presence of the bromotitanium diphenoletatcomplex 12, complete monomer conversion was achieved, affording a polymer with $M_n$ of ca. 5.0 kDa with narrow dispersity (run 16).

On the other hand, the iodo-congener only allowed for 37% monomer conversion affording low molecular weight species.

ε-CL/δ-VL co-polymerization

The co-polymerization of ε-CL and δ-VL was next investigated (Table 5). Moderate conversion (68%) was achieved in the presence of 1 (run 1) affording a polymer with low molecular weight and narrow polydispersity. The $^1$H NMR spectroscopic analyses of the crude reaction mixture suggested a CL:VL ratio in the copolymer of 40:60. No conversion was achieved when employing complex 3 (run 2). Low conversions, spanning from 20 to 40% were observed by using the titanocalix[8]arene complexes 4, 6, and 9 (runs 3-5). In all cases, the CL:VL ratio was found to be ca. 1:1. However, the molecular weights of such copolymers were too low to be detected by SEC, suggesting the occurrence of undesirable transesterification side-reactions resulting in the formation of light oligomers. Finally, good conversion was achieved by using 11 (81%, run 6). Similar to 1, the catalyst was shown to incorporate ε-CL and δ-VL in 1:1 ratio. The average sequence length for CL was found to be 2.46 while the value for VL was 1.69, as observed by $^{13}$C NMR spectroscopy (Supporting Information, Figure S17 and equations S1-3). [26] The randomness degree for the co-polymer was 1.0, compatible with a purely random copolymer. [26a]

Table 3: ROP of δ-valerolactone using complexes 1, 3, 4, 6, 9 and 11-13

| Run | Catalyst | δ-VL:Ti:BnOH | T (°C) | Time (h) | Conversion (%) | $M_n$ | $M_w$ | $M_n/M_w$ |
|-----|----------|-------------|--------|----------|----------------|-------|-------|-----------|
| 1   | 1        | 500:1:3     | 80     | 24       | 18             |       |       |           |
| 2   | 1        | 500:1:3     | 80     | 1        | none           |       |       |           |
| 3   | 6        | 250:1:3     | 130    | 24       | 45.8           | 6,360 | 3,930 | 1.13      |
| 4*  | 6        | 500:1:3     | 130    | 24       | none           |       |       |           |
| 5   | 3        | 250:1:4     | 130    | 24       | none           | -     | -     | -         |
| 6   | 4        | 500:1:2     | 80     | 24       | none           |       |       |           |
| 7   | 4        | 500:1:2     | 80     | 1        | none           |       |       |           |
| 8   | 6        | 250:1:1     | 130    | 24       | none           |       |       |           |
| 9   | 250:1:1  | 130        | 1      | none     |                |       |       |           |
| 10  | 5        | 500:1:2     | 80     | 24       | 5.1            |       |       |           |
| 11  | 5        | 500:1:2     | 80     | 1        | none           |       |       |           |
| 12  | 6        | 250:1:1     | 130    | 24       | none           |       |       |           |
| 13  | 6        | 250:1:1     | 130    | 1        | none           |       |       |           |
| 14  | 9        | 250:1:1     | 130    | 24       | 65.4           | 15,160| 16,480| 1.43      |
| 15  | 250:1:1  | 130        | 1      | none     |                |       |       |           |
| 16  | 11       | 250:1:2     | 130    | 24       | 69.6           | 13,000| 8,820 | 1.37      |
| 17  | 250:1:2  | 130        | 1      | none     |                |       |       |           |
| 18  | 12       | 250:1:2     | 80     | 24       | 52             | 6,710 | 8,120 | 1.92      |
| 19  | 250:1:2  | 80         | 24     | 64       | 6,710           | 8,120 | 1.92  |           |
| 20  | 13       | 250:1:2     | 80     | 24       | 41             | 5,590 | 6,740 | 1.14      |

a Determined by $^1$H NMR spectroscopy on crude reaction mixture. b From GPC. c Calculated from $\left(\dfrac{[\text{Monomer}]_0}{[\text{OH}]_0}\right) \times \text{conv.} \times \text{Monomer molecular weight} + \text{Molecular weight of BnOH}. d Reaction performed in air.
Table 4. ROP of rac-lactide using complexes 1, 3, 4, 6, 9 and 11-13.

| Run | Catalyst | r-LA:Ti:BnOH | T (°C) | Time (h) | Conversiona (%) | Mn,b,c | Mw/Mn,d |
|-----|----------|--------------|--------|----------|----------------|--------|----------|
| 1   | 1        | 500:1:3      | 130    | 24       | 87             | 8,190  | 21,000   | 1.29    |
| 2   | 1        | 500:1:3      | 130    | 1        | 33             |        |          |         |
| 3   | 3        | 250:1:4      | 130    | 24       | none           | -      | -        | -       |
| 4   | 3        | 500:1:2      | 130    | 24       | none           | -      | -        | -       |
| 5   | 4        | 500:1:2      | 130    | 1        | 33             | -      | -        | -       |
| 6   | 4        | 250:1:1      | 130    | 24       | none           | -      | -        | -       |
| 7   | 4        | 250:1:1      | 130    | 1        | none           | -      | -        | -       |
| 8   | 6        | 500:1:2      | 130    | 24       | none           | -      | -        | -       |
| 9   | 6        | 500:1:2      | 130    | 1        | none           | -      | -        | -       |
| 10  | 6        | 250:1:1      | 130    | 24       | none           | -      | -        | -       |
| 11  | 6        | 250:1:1      | 130    | 1        | none           | -      | -        | -       |
| 12  | 9        | 250:1:1      | 130    | 24       | none           | -      | -        | -       |
| 13  | 9        | 250:1:1      | 130    | 1        | none           | -      | -        | -       |
| 14  | 11       | 250:1:1      | 130    | 24       | 8.2           |        |          |         |
| 15  | 11       | 250:1:1      | 130    | 1        | none           | -      | -        | -       |
| 16  | 12       | 250:1:2      | 130    | 24       | >99           | 4,980  | 21,650   | 1.20    |
| 17  | 13       | 250:1:2      | 130    | 24       | liquid oligomers |

a Determined by 1H NMR spectroscopy on crude reaction mixture. b From GPC. c Values corrected considering Mark–Houwink factor (0.58) from polystyrene standards in THF. d Calculated from ([Monomer]0/[OH]0) × conv. (%) × Monomer molecular weight + Molecular weight of BnOH.

Table 5. ε-CL/δ-VL Co-polymerization using complexes 1, 3, 4, 6, 9 and 11-13.

| Run | Catalyst | ε-CL:δ-VL:Ti:BnOH | Conversiona (%) | CL/VLa | Mn,b,c | Mw/Mn,c |
|-----|----------|-------------------|-----------------|--------|--------|---------|
| 1   | 1        | 250:250:1:3       | 67.6            | 40:60  | 7,770  | 1.19    |
| 2   | 3        | 250:250:1:4       | none            | -      | nd     | nd      |
| 3   | 4        | 250:250:1:1       | 29.9            | 50:50  | nd     | nd      |
| 4   | 6        | 250:250:1:1       | 41.9            | 50:50  | nd     | nd      |
| 5   | 9        | 250:250:1:1       | 22.2            | 50:50  | nd     | nd      |
| 6   | 11       | 250:250:1:1       | 8.2             |        |        |         |
| 7   | 12       | 250:250:1:2       | >99             | 55:45  | 12,480 | 1.70    |
| 8   | 13       | 250:250:1:2       | >99             | 60:40  | 13,360 | 1.84    |

a Determined by 1H NMR spectroscopy on the crude reaction mixture based on ε-CL. b Determined by 13C NMR. c From GPC. d Values corrected considering Mark–Houwink factor [(Mn × %CL × 0.56) + (Mn × %VL)] from polystyrene standards in THF.

In the presence of the bi-phenolate complexes 12 and 13, complete conversion of ε-CL was observed (runs 7 and 8), affording co-polymers with Mn spanning from 12 to 14 kDa with rather poor control (Mw/Mn, ca. 1.75). Also in this case, the co-polymer composition was analyzed by 13C NMR spectroscopy. For the polymer isolated with 12, the average sequence length was 2.10 and 2.05 for CL and VL, respectively (Supporting Information, figure S18), with a randomness degree of 0.97, compatible with a purely random co-polymer. [26a] A similar outcome was achieved with complex 13; in fact, the average sequence lengths were 2.50 and 1.82 for CL and CL, respectively, with a randomness degree of 0.95 (Supporting Information, figure S19).

ε-CL/r-LA co-polymerization

None of the complexes proved to be active in the co-polymerization of ε-CL and r-LA at 130 °C. In most cases, both monomers were unreacted after 24 h. Nevertheless, 14% conversion of r-LA in PLA was achieved in the presence of 1, as highlighted by 1H NMR spectroscopy on the crude reaction mixture (See Figure S20, ESI).
Conclusion
The treatment of L^1H_8 with [TiCl_4] afforded complex 1.4.5MeCN, in which two pseudo octahedral titanium centres are bound to one calix[6]arene. A similar preparation conducted in THF resulted in the THF ring-opened product 2.4MeCN, where L^2H = p-tert-butylcalix[4]areneH_4. In the case of TiF_4 (3 equiv.), reaction with L^2H afforded the orange/red complex 3.6.5MeCN, in which two TiF_2 diamonds, which bridge the calixarenes, whilst two fluoride ions bridge the two diamonds. The reaction between L^2H, with [TiCl_4] led to 4.1.5MeCN and, from a similar preparation, to the co-crystallized complex 5.11MeCN. Extension of the L^2H chemistry to [TiBr_4] afforded, depending on the stoichiometry, 6.6MeCN or 7.7.5MeCN. Interestingly, the use of [TiF_4] afforded complexes containing Ca^2+ and Na^2+, most likely deriving from drying agents, namely 8.14MeCN), 9.7MeCN or 10.15.5MeCN. By using TiI_6, the ladder 11: 7.25CH_2Cl_2 was isolated. These complexes have been tested as catalysts in the ring opening polymerization (ROP) of e-CL, δ-VL and r-LA, both in air and N_2. In the case of e-CL, high temperatures (130 °C) over 24 h were required to achieve reasonable conversions for 1, 9 and 11 (3 and 6 were inactive). However, these metallocalix[n]arenes are out-performed by the diphenolates 12 and 13, which doubtless reflects the accessibility of the metal centres in the latter. In the case of δ-VL, the salts 9 and 10 as well as 12 and 13 perform best, whilst for r-LA, 1, 12 and to a lesser extent 11, 13 were active. For the copolymerization of e-CL with δ-VL reasonable activity was exhibited by 1 and 11, whilst conversions lower than 40% were observed with the other complexes; all afforded low molecular weight polymers. The copolymerization of e-CL with r-LA was unsuccessful regardless of the catalyst employed. In general for these systems, more accessible metal centres (e.g. 1, 12 and 13) and the formation of salts (e.g. 9 – 11) favours improved performance.

Experimental Section
General: All manipulations were carried out under an atmosphere of dry nitrogen using conventional Schlenk and cannula techniques or in a conventional nitrogen-filled glove box. Hexane and toluene was refluxed over sodium. Acetonitrile was refluxed over calcium hydride. All solvents were distilled and degassed prior to use. IR spectra (nujol mulls, KBr windows) were recorded on a Nicolet AVATAR 360 FT IR spectrometer; 1H NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400 MHz or a Gemini 300 NMR spectrometer or a Bruker Advance DPX-300 spectrometer at 300 MHz. The 1H NMR spectra were calibrated against the residual protio impurity of the deuterated solvent. Elemental analyses were performed by the elemental analysis service at the London Metropolitan University and in the Department of Chemistry, the University of Hull. All chemicals were purchased from either Sigma Aldrich or TCI UK.

Synthesis of [TiCl(C=NM(CN)Me)_2] (LCl)(L^1H)]·4.5 MeCN
To L^1H_8 (2.00 g, 2.05 mmol) in toluene (30 mL) was added [TiCl_4] (0.71 mL, 6.50 mmol) and the system was refluxed for 12 h. On cooling, the volatiles were removed in vacuo, and the residue was extracted into MeCN (30 mL). On standing at ambient temperature (ca. 10 °C) for 2 days, orange crystals of 1 formed. Yield 1.80 g, 64%. Sample dried under reduced pressure for 12 h (-4.5 MeCN). C_{34}H_{17}Cl_4N_2O_7Ti_4 requires C 66.51, H 6.88, N 2.73%. Found C 66.59, H 7.22, N 2.21%. IR: 3596w, 2727w, 2326w, 1635w, 1569w, 1564m, 1296m, 1259s, 1208s, 1121s, 1096s, 1022s, 928, 884s, 859m, 799s, 766m. 1H NMR (C6D_6): 3H NMR (CDCl_3, 298K) δ: 7.15-7.66 (m, 12H, aryH), 6.36 (s, 1H, aryOH), 6.20 (s, 1H, Ti-OH), 4.74 (d, 2H, J = 12 Hz, endo-CH_2), 4.19 (d, 1H, J = 12 Hz, endo-CH_2), 4.33 (d, 1H, J = 12 Hz, endo-CH_2), 4.11 (d, 1H, J = 12 Hz, endo-CH_2), 3.57 (d, 4H, J = 12 Hz, exo-CH_2), 2.98 (d, 1H, J = 12 Hz, exo-CH_2), 2.01 (s, 12H, 4 uncoordinated MeCN), 1.29-1.01 (m, 54H, C(CH_3)_3), 0.50 (s, 6H, 2 coordinated MeCN).

Synthesis of [(TiCl)(μ-Cl)(μ-L)]·6.5MeCN (3-6.5MeCN) Crystals of complex 2 suitable for X ray analysis were obtained in low yield (<5%) from the preparation of 1. Due to the limited amount of sample (~5mg), only 1H NMR spectroscopy analysis could be performed. 1H NMR (DCl_3, 298K) δ: 7.20 – 7.05 (m, 16H aryH), 5.43 (d, 4H, J = 13 Hz, endo-CH_2), 5.15 (d, 4H, J = 13 Hz, endo-CH_2), 4.97 (m, 4H, CHC(CH_2CH_2OCl)_2), 4.88 (m, 4H, ClC(CH_2CH_2OCl)_2), 4.10 (m, 4H, exo-CH_2), 2.24 (m, 4H, ClC(CH_2CH_2OCl)_2), 1.98 (m, 4H, ClC(CH_2CH_2OCl)_2), 1.56 – 1.23 (m, 72H C(CH_3)_2).

Synthesis of [(TiF_2)(μ-F)(μ-L)]·6.5MeCN (3-6.5MeCN) To L^1H_8 (2.00 g, 2.05 mmol) in toluene (30 mL) was added [TiF_4] (0.76 g, 6.14 mmol) and the system was refluxed for 12 h. On cooling, the volatiles were removed in vacuo, and the residue was extracted into MeCN (30 mL). On standing at ambient temperature at 0 °C for 2 days, orange/red crystals of 3 formed. Yield 1.75 g, 68%. C_{212}H_{368}F_4O_2Ti_3MeCN (sample dried in vacuo for 2h, -3.5MeCN) requires C 70.07, H 7.12, N 1.78%. Found C 68.82, H 7.18, N 1.29%. IR: 3442bs, 2727w, 2671w, 1636m, 1600m, 1417m, 1392s, 1364s, 1297m, 1260s, 1201s, 1101s, 1020s, 932m, 886m, 860m, 799s, 776w, 680w, 588w, 559w, 545w, 463w, 438w.H NMR (CDCl_3) δ:7.24 (s, 8H, ArH), 7.12 (s, 8H, ArH), 6.99 (s, 8H, ArH), 5.17 (d, 12H, 15H, endo-CH_2), 4.00 (bs, 2H, -OH), 3.18 (d, 15 Hz, 12H, exo-CH_2), 2.00 (s, 18H, 6 coordinated MeCN), 1.26 (s, 54H, C(CH_3)_2), 1.16 (s, 54H, C(CH_3)_2). 19F NMR (CDCl_3) δ: -2.13 (q, J = 49 Hz, 2F, Ti-F-Ti), -15.96 (t, J = 46 Hz,4F, TiF_2).

Synthesis of [(TiCl_2)(μ-Cl)(μ-L)]·1.5MeCN (4-1.5MeCN) As for 1, but using L^1H_8 (2.00 g, 1.54 mmol) and [TiCl_4] (6.50 mL, 1.0M in CH_2Cl_2, 6.50 mmol) affording 4 as small red prisms. Yield 2.13 g, 77%. Sample dried in vacuo for 2h (~1.5MeCN) C_{105}H_{222}Cl_2N_2O_7Ti_4 requires C 63.60, H 6.38, N 1.61%. Found C 62.87, H 6.71, N 1.43%. IR: 2319w, 2308w, 2289w, 2257w, 1648m, 1596s, 1393m, 1364m, 1291m, 1256s, 1196s, 1122m, 1105m, 1028m, 933s, 887s, 878s, 862s, 855s, 796m, 772w,
1.0M in CH

Synthesis of [Ti$_2$CaF$_{20}$(OH)$_3$MeCN]$_2$(L$_1$)$_2$-14MeCN (8-14MeCN)

L$_2$H$_2$ (2.00 g, 1.54 mmol) and [TiF$_4$]$_2$ (0.76 g, 6.16 mmol) were combined in toluene (30 mL) and the system was refluxed for 12 h. On cooling, volatiles were removed in vacuo, and the residue was extracted into MeCN (30 mL). Prolonged standing at 0 °C afforded 8 as red, blade-like crystals. Yield: 1.87 g, 58%. The sample was dried under reduced pressure for 16 h. C$_{184}$H$_{234.0}$Ca$_{20}$F$_{20}$Na$_{17}$Ti$_{12}$·(14MeCN) requires C 61.13, H 6.49, N 1.54%. Found: C 60.73, H 6.34, N 1.89%. IR: 1648w, 1303w, 1261s, 1199w, 1095s, 1020s, 929w, 875w, 859w, 800s, 753w, 722w, 660w. H NMR (CD$_2$)$_2$: 7.35-7.12 (m, 16H, ArH), 7.10-6.98 (m, 16H, ArH), 7.50 (m, 8H, endo-CH$_2$), 5.08-4.95 (m, 4H endo-CH$_2$), 4.02-3.82 (m, 4H, exo-CH$_2$), 3.43 (m, 4H, exo-CH$_2$), 3.26 (m, 4H, exo-CH$_2$). 3.08 (m, 8H, exo-CH$_2$), 1.40-1.21 (m, 72H, C(C$_6$H$_5$)). 1.20-1.07 (m, 72H, C(C$_6$H$_5$)). 0.50 (s, 12H, 24 coordinated MeCN). 2H 0.5 (d, J = 13 Hz, 2H, endo-CH$_2$), 2.28-2.15 (m, 16H, C(C$_6$H$_5$)), 1.32-1.28 (m, 72H, C(C$_6$H$_5$)), 0.54 (s, 18H, coordinated MeCN).

Synthesis of [Na(Me(NCMe)$_2$)$_2$][Ti$_4$Ca$_2$F$_{20}$Na$_{12}$O$_{10}$L$_2$]·7 MeCN (9-7MeCN)

As for 8, affording 9 as red blade-like crystals. Yield: 46%. C$_{176}$H$_{236}$Ca$_{20}$F$_{20}$Na$_{17}$Ti$_{12}$·9(H$_2$N) requires C 61.41, H 6.21, N 2.64%. Found C 60.65, H 6.69, N 2.48%. IR: 1651w, 1300w, 1257s, 1200w, 1089s, 1015s, 925w, 871w, 857w, 798s, 756w, 727w, 663w. H NMR (CD$_2$)$_2$: 7.34-7.09 (m, 16H, ArH), 7.03-6.86 (m, 16H, ArH), 6.26-6.09 (m, 4H exo-CH$_2$), 5.94-5.80 (m, 8H, endo-CH$_2$), 5.21-4.93 (m, 4H, endo-CH$_2$), 4.50-4.44 (m, 4H, exo-CH$_2$), 4.40-4.35 (m, 4H, exo-CH$_2$), 4.19-4.15 (m, 4H, exo-CH$_2$), 3.99-3.84 (m, 4H, exo-CH$_2$), 2.11 (s, 11H, 7 coordinated MeCN). 1H MeCN 1.41-1.37 (m, 72H, C(C$_6$H$_5$)), 1.32-1.28 (m, 72H, C(C$_6$H$_5$)), 0.58 (s, 6H, 2 coordinated MeCN). 2H NMR (CD$_2$)$_2$: 3.50-3.50 (bs), -6.72 (bs, 2F), -6.90 (bs, 2F), -8.04 (bs, 2F), -11.40 (bs, 2F), -13.74 (bs, 2F), -17.40 (bs, 2F), -19.61 (bs, 2F), -21.94 (bs, 2F), -27.32 (bs, 2F).

Synthesis of [Na$_2$[(C$_{180}$H$_{226}$F$_{20}$Na$_{17}$O$_{16}$Ti$_{8}$]C$_{177}$H$_{208.5}$F$_{20}$Na$_{17}$O$_{16}$Ti$_{8}$]C$_{15}$C$_{2}$H$_{2}$N$_{3}$(10-15.5MeCN)

As for 8, except that both the toluene and acetonitrile were dried over activated molecular sieves, to afford 10 in 61% yield. Sample dried under reduced pressure for 3 h (7.5MeCN). C$_{184}$H$_{234.0}$F$_{20}$Na$_{17}$O$_{16}$Ti$_{8}$(9MeCN) requires C 61.37, H 6.18, N 2.01%. Found: C 61.96, H 6.42, N 2.11%. IR: 2727w, 1598w, 1301w, 1260s, 1197m, 1020s, 929m, 855m, 798s, 752m, 102w, 672w, 619m, 590m, 561m, 541m, 500m. H NMR (CD$_1$(L$_2$)) requires C 7.64-7.57 (m, 16H, ArH), 7.30-7.26 (m, 16H, ArH), 4.67-4.62 (m, 4H, endo-CH$_2$), 4.52-4.45 (m, 4H, endo-CH$_2$), 3.99-3.96 (m, 8H, endo-CH$_2$), 3.44-3.39 (m, 8H, exo-CH$_2$), 3.24-3.21 (m, 8H, exo-CH$_2$), 2.94-2.90 (m, 4H, exo-CH$_2$), 1.30-1.19 (m, 72H, C(C$_6$H$_5$)), 1.09-0.98 (m, 72H, C(C$_6$H$_5$)). 2H NMR (CD$_1$(L$_2$)): 3.78 (m, 2F), -6.78 (m, 1F), -8.61 (m, 2F), -10.0 (m, 2F), -11.7 (m, 4F), -13.5 (m, 2F), -15.2 (m, 1F), -19.9 (m, 2F), -23.2 (m, 2F), -32.3 (m, 2F).
Synthesis of [(TiI)₂(TiNCMe)₂(μ₃-O)₂(L²)] 7.25CH₂Cl₂ (11.7-25CH₂Cl₂)

As for 1, but using L²H₈ (2.00 g, 1.54 mmol) and [TiI₄] (3.59 g, 6.46 mmol). Extraction into CH₂Cl₂ (30 mL) afforded upon prolonged standing at 0 °C red blocks of (11.7-25CH₂Cl₂). Yield: 2.22 g, 53%. C₈₀H₁₄₂O₈Cl₁₄I₁₄Ti₂ 7.25(CH₂Cl₂) C 44.08, H 4.63, N 0.57%. IR: 2720 w, 1650 w, 1600 w, 1100 m, 925 s. Found: C 42.80, H 4.87, N 0.55%. IR: 2720 w, 1650 w, 1600 w, 1100 m, 925 s.

Synthesis of [TiBr₂(6,6′-(ethane-1,1-diyl)bis(2,4-di-tert-butylphenolate))] hexane (12 hexane)

To a solution of 6,6′-(ethane-1,1-diyl)bis(2,4-di-tert-butylphenolate) (1.00 g, 2.28 mmol) in hexane (30 mL), TiBr₄ (0.84 g, 2.28 mmol) was added and the mixture was stirred at 60 °C for 16 h. Upon cooling to room temperature, 12 was obtained as a red solid, which was recovered by filtration, washed with hexane (2 x 10 mL) and dried in vacuum at room temperature for 16 h. The product 12, recrystallized from hexane (2 x 10 mL) and dried in vacuum at room temperature for 16 h, showed spectral data consistent with the structure. Yield 1.30 g, 88%. C₄₄H₄₄Br₂O₂Ti requires C 55.92, H 6.88 %. Found C 55.69, H 7.05 %. ¹H NMR (CDCl₃): δ: 7.45 (d, J = 2.5 Hz, 2H, ArH), 7.20 (d, J = 2.5 Hz, 2H, ArH), 4.15 (q, J = 6.6 Hz, 1H, CH(CH₃)), 1.74 (d, J = 6.9 Hz, 3H, CH₃), 1.51 (s, 18H, C(CH₃)₃), 1.32 (s, 18H, C(CH₃)₃). IR: 1223 s, 1198 s, 1100 w, 925 s. There are no conflicts to declare.
Table 6. Crystallographic Data

| Compound | 1·4.5(C$_7$H$_8$N) | 2·4(C$_7$H$_8$N) | 3·6.5(C$_7$H$_8$N) | 4·1.5(C$_7$H$_8$N) |
|----------|-------------------|-----------------|------------------|------------------|
| Formula  | [C$_7$H$_7$Cl$_2$N$_2$O$_3$Ti$_2$]·4.5(C$_2$H$_3$N) | C$_{150}$H$_{125}$Cl$_3$N$_3$O$_6$Ti$_2$·4(C$_2$H$_3$N) | C$_{132}$H$_{125}$F$_6$O$_6$Ti$_4$·6.5(C$_2$H$_3$N) | C$_{92}$H$_{110}$Cl$_4$N$_2$O$_6$Ti$_4$·1.5(C$_2$H$_3$N) |
| Formula weight | 2748.90 | 2045.64 | 2509.02 | 1798.79 |
| Crystal system | Triclinic | Triclinic | Monoclinic | Orthorhombic |
| Space group | P$ar{i}$ | P$ar{i}$ | C$_2$/c | P$_2_1_2_1_2_1$ |
| a (Å) | 12.7071(4) | 11.1401(2) | 24.7656(7) | 18.7623(3) |
| b (Å) | 24.5925(4) | 15.00590(15) | 22.6045(5) | 19.3331(3) |
| c (Å) | 25.2999(7) | 16.5752(3) | 26.9512(3) | 26.9512(3) |
| α (º) | 104.399(2) | 104.2611(12) | 90 | 90 |
| β (º) | 96.177(2) | 93.0977(15) | 90.923(2) | 90 |
| γ (º) | 91.761(2) | 98.7122(13) | 90 | 90 |
| V (Å$^3$) | 7599.8(3) | 2642.36(7) | 13801.2(6) | 9776.1(2) |
| Z | 2 | 1 | 4 | 4 |
| Temperature (K) | 100(2) | 100(2) | 100(2) | 100(2) |
| Wavelength, λ (Å) | 1.54178 | 1.54178 | 0.71073 | 1.54178 |
| Calculated density (g.cm$^{-3}$) | 1.201 | 1.286 | 1.208 | 1.222 |
| Absorption coefficient, μ (mm$^{-1}$) | 3.17 | 3.90 | 0.29 | 4.13 |
| Transmission factors (min./max.) | 0.694, 1.000 | 0.917, 1.000 | 0.568, 1.000 | 0.724, 1.000 |
| Crystal size (mm$^3$) | 0.26 × 0.05 × 0.01 | 0.07 × 0.06 × 0.05 | 0.19 × 0.10 × 0.06 | 0.10 × 0.05 × 0.02 |
| θ(max) (º) | 68.2 | 68.3 | 27.5 | 68.2 |
| Reflections measured | 102365 | 99465 | 69296 | 94785 |
| Unique reflections | 27528 | 19474 | 15792 | 17801 |
| R$_{int}$ | 0.103 | 0.024 | 0.082 | 0.049 |
| Reflections with F$^2$ > 2σ(F$^2$) | 14620 | 17743 | 9515 | 15039 |
| Number of parameters | 1964 | 645 | 824 | 1175 |
| R$_1$ (F$^2$ > 2σ(F$^2$)) | 0.126 | 0.067 | 0.083 | 0.063 |
| wR$_2$ (all data) | 0.380 | 0.190 | 0.245 | 0.180 |
| GOOF, S | 1.03 | 1.05 | 1.07 | 1.02 |
| Largest difference peak and hole (e Å$^{-3}$) | 1.41 and −0.84 | 2.55 and −1.20 | 0.91 and −0.70 | 0.94 and −0.48 |
| Compound | Formula | Formula weight | Crystal system | Space group | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) | V (Å³) | Z | Temperature (K) | Wavelength, λ (Å) | Calculated density (g cm⁻³) | Absorption coefficient, μ (mm⁻¹) | Transmission factors (min./max.) | Crystal size (mm³) | δ(max) (°) | Reflections measured | Unique reflections | Rint | wR₂ (all data) | GOOF, S | Largest difference peak and hole (e Å⁻³) |
|----------|---------|---------------|----------------|-------------|-------|-------|-------|-------|-------|-------|-------|-------|-----|----------------|------------------|----------------------|------------------------|------------------------|----------------|----------------|----------------------|----------------|-------|----------------|---------|----------------|----------------|
| 5·(H₂O)·11(C₆H₅N) | [C₉₀H₁₁₀Cl₄N₂O₁₀Ti₄·OH₂·11(C₆H₅N)] | 4078.23 | Triclinic | Pī | 18.0637(2) | 21.02305(10) | 21.5584(2) | 103.4502(9) | 90 | 90 | 11168.9(2) | 2 | 100(2) | 1.54178 | 1.213 | 3.62 | 0.757, 1.000 | 0.10 × 0.10 × 0.03 | 68.3 | 204131 | 40624 | 0.075 | 0.027 | 0.106 | 1.96 and −0.74 |
| 6·6(C₆H₅N) | C₉₀H₁₁₀Br₄N₂O₁₀Ti₄·6(C₆H₅N) | 2161.38 | Monoclinic | P2₁/c | 20.6914(3) | 17.27686(8) | 29.70228(14) | 97.2290(8) | 90 | 102.5511(5) | 10530.42(9) | 4 | 100(2) | 1.54178 | 1.363 | 4.74 | 0.595, 1.000 | 0.24 × 0.14 × 0.08 | 68.3 | 100958 | 19224 | 0.027 | 0.036 | 0.242 | 0.89 and −0.66 |
| 7·7.5(C₂H₅N) | C₈₀H₁₁₀Br₄N₂O₁₀Ti₄·7.5(C₂H₅N) | 2446.07 | Monoclinic | P2₁/n | 21.6443(2) | 21.5584(2) | 95.7763(7) | 90 | 90 | 12497.5(2) | 2 | 100(2) | 1.54178 | 1.300 | 4.28 | 0.539, 1.000 | 0.19 × 0.09 × 0.01 | 68.2 | 126455 | 22797 | 0.054 | 0.091 | 0.293 | 2.76 and −1.42 |
| 8·14(C₂H₅N) | C₁₈₄H₂₃₄Cl₂₂N₉O₂₀Ti₈·14(C₂H₅N) | 4195.75 | Monoclinic | P2₁/m | 23.6904(10) | 20.9093(17) | 23.7763(7) | 90 | 90 | 11237.6(11) | 2 | 100(2) | 0.71073 | 1.240 | 0.37 | 0.373, 1.000 | 0.17 × 0.04 × 0.02 | 27.5 | 108461 | 26376 | 0.151 | 1.086 | 0.399 | 1.15 and −0.68 |
### Notes and references

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Please do not adjust margins
\[ \text{TiX}_4 + \text{Compound} \xrightarrow{\Delta, \text{Toluene} (\text{dried over Na})} 12 \text{ new structures} \]

\[ \text{i) Workup in MeCN (dried over CaH}_2) \]

\[ X = \text{F, Cl, Br, I} \]

\[ n = 3, 5 \]

**ROP of cyclic esters**

- **Na/Ca uptake from drying agents**

- **Biodegradable Polymers**