Vanadium complexes derived from oxacalix[6]arenes: structural studies and use in the ring opening homo-/co-polymerization of ε-caprolactone/δ-valerolactone and ethylene polymerization†

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Reaction of Na[VO(tBuO)4] (generated in situ from VOCl3 and NaOtBu) with p-tertbutyltetrahydroxidocalix[6]areneH4 (LpH4) afforded, after work-up (in MeCN), the mixed-metal complex [VO2(p-O)2MeCN(MeCN)2]-5(MeCN) (L5MeCN), whilst the oxo complex [VO(L3)L2]2 (L2MeCN) was isolated via the use of [VO(OH)]n observes. Reaction of LpH4 with [V(Np-Ch2C6H4)OEt]n afforded the complex [V(Np-Ch2C6H4)O-Et]n (3-7MeCN-0.5CH2Cl2). Use of similar methodology afforded the imido complexes [V(Np-Rc6H4)2]n (R = O Me(-)), CF3 (-), Cl (-) on one occasion, reaction of [V(Np-Ch2C6H)OEt]n with LpH4 afforded the product [VOL2]-4MeCN (8-4MeCN) (L2 = 2-(p-CH3-C6H4NCH)-4-tBuC6H2O-6-CH2)-4-tBuC6(OH)4 (L1) has been cleaved. For comparative catalytic ring opening polymerization (ROP) studies, the known complexes [VOL]n (L1 = oxacalix[3]arenes) (I), [V(Np-Ch2C6H4)OEt]n (II), [Li(MeCN)4] [V2O5LiMeCN(LH)2] (III) and [V2O5H2] (L3H2) = p-tert-butyldcalix[6]areneH2) (IV) have also been prepared. ROP studies, with or without external alcohol present, indicated that complexes 1 to 8 exhibited moderate to good conversions for ε-Cl, ε-VL and the co-polymerization thereof. Within the imido series, a positive influence was observed when electron withdrawing substituents were present. These systems afforded relatively low molecular weight products and were also inactive toward the ROP of rac-lactide. In the case of ethylene polymerization, complexes 3, 5 and 7 exhibited highest activity when screened in the presence of dimethylaminochloride/ethyltrichloroacetate; the activity of 4 was much lower. The products were highly linear polyethylene with Mw in the range 74–120 × 10^3 Da.

Introduction

The need for new environmentally friendly plastics has been highlighted by on-going global pollution issues, however traditional plastics, when used and disposed of correctly, still have a large part to play in society. Indeed, the recent COVID19 outbreak is a good illustration of our dependence on plastics, where there was widespread demand for the use of plastic-based face masks.1 Metal catalysts play a central role in the production of both petroleum-based plastics (α-olefin polymerization) and biodegradable polymers formed via the ring opening polymerization (ROP) of cyclic esters.2 For both processes, manipulation of the catalyst properties can be achieved by variation of the metal-bound groups, and this allows for control over both catalytic activity and polymer properties. It is also important that the catalytic metal centre employed is cheap and non-toxic. With this in mind, a number of earth-abundant metals have been employed as the reactive metal centre in both polymerization processes.1,3 Furthermore, results using vanadium-based systems indicate this metal also has potential in this

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area, and it is noteworthy that reports on the effect of imido ligand variation in vanadium-based systems have appeared for studies on oligo/polymerization of ethylene, ethylene/propane copolymerization and ethylene/olefin copolymerization. The ligands in the pre-catalyst can take a number of forms, selected in-part for their ability to impose some stability to the catalytically active species. In α-olefin polymerization, an external alkylating co-catalyst is typically employed to form a metal-alkyl [M–R] species, whilst in ROP, the generation of metal alkoxide [M–OR] species is favoured. Calix[n]arenes, which are phenolic macrocycles, have shown potential in a variety of catalytic applications. By variation of $n$, the number of phenolic groups, calix[n]arenes can act as platforms for binding multiple metal centres. In our previous work, a series of vanadium-based calix[n]arene complexes were structurally identified, and by changing the calixarene bridging group from a methylene (–CH$_2$–) to a dimethyleneoxa group (–CH$_2$OCH$_2$–), vanadium complexes with superior catalytic performance for both α-olefin homo- and co-polymerization over related methylene-bridged systems were obtained. These vanadium studies previously focused on oxacalix[3]arene derivatives, however larger oxacalix[n]arenes are known. Herein, we investigate the use of the $p$-tert-butyltetramethoxycalix[6]$[$arene$]_n$-$H_6$-$L_1$-$H_6$-$L_8$-$Na_2$-$[L_1](MeCN)_4$-$5$-$MeCN$ derived systems (Chart 1) in both the ROP of the cyclic esters $\varepsilon$-caprolactone and $\delta$-valerolactone, and the copolymerization thereof, and for the polymerization of ethylene. Results are compared versus known vanadium catalysts bearing either $p$-tert-butylhexahomotrioxacalix[3] arene$H_8$ or $p$-tert-butylcalix[6 and 8]arene$H_8$-$H_6$-$H_8$-$L_8$-$Na_2$-$[L_1](MeCN)_4$-$5$-$MeCN$ and $\varepsilon$-caprolactone, PCL and PVL are favoured polymers given their biodegradability and the fact that they are considered as potential environmentally friendly commodity plastics.

Results and discussion

Syntheses and solid-state structures

Oxo complexes. The heterobimetallic vanadium(V)/alkali metal reagent [NaVO(OtBu)$_4$]$_2$ was synthesised by an adaptation of a procedure described by Wilkinson and co-workers, whereby [VOCl$_3$] and four equivalents of NaOtBu were stirred in diethyl ether (or THF) at $-78$ °C for 12 h. In situ reaction of this vanadyl salt (two equivalents) with $p$-tert-butyltetramethoxycalix[6]$[$arene$]_n$-$H_6$-$L_1$-$H_6$-$L_8$-$Na_2$-$[L_1](MeCN)_4$-$5$-$MeCN$ (1:5MeCN), and the molecular structure of 1:5MeCN is shown in Fig. 1, with selected bond lengths and angles given in the caption. The complex contains two trigonal bipyrimal vanadyl centres, for which the V=O5 bond length is typical at 1.588(3) Å, linked via near linear (171.8(2)°) V–O11–V bonding. Each vanadium is further coordinated by three phenoxide oxygens of the oxacalix[6]arene, with longer bonding (ca. 1.95 Å) observed to each of the bridging calixarene oxygens (O2 and O8) which are also involved in

![Chart 1](Image 14x290 to 26x354)

**Chart 1** The pre-catalysts 1–8 prepared herein.

![Chart 2](Image 14x290 to 26x354)

**Chart 2** Known pre-catalysts I–IV used herein.

![Fig. 1](Image 14x290 to 26x354)

**Fig. 1** Molecular structure of [(VO)$_4$($\mu$-O)Na$_2$(L)$^-$][MeCN]$_4$-$5$(MeCN) (1:5MeCN) (H atoms and free MeCN molecules are omitted for clarity). Selected bond lengths (Å) and angles (°): V1–O1 1.832(3), V1–O2 1.946(3), V1–O3 1.949(3), V1–O9 1.588(5), V1–O11 1.825(3), Na1–O1 2.231(3), Na1–O3 2.427(4), Na1–O4 2.232(4), Na1–N2 2.459(6), Na1–O8 2.396(5); O1–V1–O2 87.74(14), O1–V1–O9 112.40(16), O2–V1–O8 176.37(14), V1–O11–V2 171.8(2), O2–Na1–O8 107.28(13).
bonding to a 5-coordinate sodium cation, with the latter (Na1 and Na2) each bonding to two of the phenoxy oxygens and the oxygen of the dimethyleneoxa bridge. Two acetonitrile ligands complete the bonding at each sodium centre.

Reaction of [VO(OnPr)3] (4 equivalents) with L1H6, led, after work-up, to the blue complex \{[VO]L1\}_6·6MeCN (2·6MeCN). The molecular structure is shown in Fig. 2, with selected bond lengths and angles given in the caption. Calixarenes bind four vanadyl centres which form a 3-step V₄O₄ ladder. Such ladders have been observed previously in titanium calixarene chemistry.13

Two of the vanadyl centres (V1) are distorted octahedral and are bound by a long V-O2 bond (2.3732(14) Å) involving the oxygen of the dimethyleneoxa bridge trans to the vanadyl group, two phenoxy (1.7934(14) and 1.8128(14) Å) and an n-proxide (V1-08 1.7869(14) Å). The other vanadyl centre (V2) is trigonal bipyramidal (r = 0.18),14 and is linked to V1 via a triply bridging oxygen O6 (Fig. 2).

**Imido complexes.** Given that the oxo group is isoelectronic with the imido group,15 and that the latter can provide a useful NMR handle and can also be varied to alter the electronics, and to a lesser degree the steric of the system,6 we also prepared a number of organoimido-containing vanadium complexes derived from L1H6. Our entry into this chemistry is via the organoimido tris-alkoxides of the type \{[V(Na)(OR)]\}_3 (R = tBu, iPr, nPr or Et) which are readily available either via the use of \{[V(NpRcH4)2Cl]_2\} and subsequent addition of KOtBu,16 or via the addition of ArNCO to [VO(OR)]_2.17 Both routes have been utilized herein.

Interaction of \{[V(Np-CH3C6H4)(OEt)3] with L1H6 led, following work-up, to the isolation of the complex \{[V(Np-CH3C6H4)2L1\}_3 (3·7MeCN·0.5CH2Cl2). Single crystals were grown from a saturated acetonitrile solution at ambient temperature and an X-ray structure determination revealed the structure shown in Fig. 3; selected bond lengths and angles are given Table 1. Each vanadium adopts a distorted squared-based pyramidal geometry with the near-linear imido ligand at the trigonal bipyramidal (r = 0.11),13 and are linked via asymmetric aryloxo bridges (of the dioxacalix[6]arene).

Replacement of the para methyl group by OMe (4), CF3 (5), Cl (6) and F (7) led to the formation of the complexes 4–7 adopting the same general dimeric structure as observed for 3 (for synthetic details see the experimental section). The geometrical parameters (Table 1), show the similarity between these molecules and the p-tolyl analogue. The molecular structures of 4–6 are given in the ESI† (Fig. S1). As reported by Maatta et al.,16 the 31V NMR shifts are very sensitive to the nature of the para substituent in such imido complexes (Fig. 4). In general, the trend observed herein is as observed by Maatta, with the electron donating groups (e.g. p-OMe) at low field versus electron withdrawing groups (e.g. p-CF3) at high field. The exception is the p-F derivative, which surprisingly is found at low field (~173.4 ppm) and we tentatively attribute this to its position in relation to the macrocycle conformation.

When the metal precursor employed was \{[V(Np-CH3C6H4)(OEt)3] with L1H6 led to the formation of small yellow prisms of [VO(L2)]_4·4MeCN (8·4MeCN) (L2 = 2-(p-

### Table 1 Selected bond lengths (Å) and angles (°) for 3–6

| Bond             | 3·7MeCN·0.5CH2Cl2 | 4·4MeCN | 5    | 6    |
|------------------|-------------------|---------|------|------|
| V1–O1            | 1.837(3)          | 1.852(15) | 1.786(4) | 1.826(4) |
| V1–O2            | 2.095(3)          | —       | —    | —    |
| V1–O3            | —                 | 1.789(14) | 1.815(4) | 1.782(4) |
| V2–O4            | —                 | 2.068(15) | 2.015(4) | 2.010(4) |
| V2–O5            | 1.839(3)          | 1.841(16) | 1.775(4) | 1.836(4) |
| V2–O7            | —                 | 1.783(15) | 1.818(4) | 1.794(4) |
| V1–N1            | 1.652(3)          | 1.656(18) | 1.645(5) | 1.665(5) |
| V1–O6            | 2.016(3)          | —       | —    | —    |
| V1–O7            | 1.786(3)          | —       | —    | —    |
| V1–O1–C1         | 123.2(2)          | 123.00(12) | 127.2(3) | 127.2(4) |
| V1–O1–C58        | 129.3(2)          | —       | —    | —    |
| V1–O8–C58        | 128.44(12)        | 120.9(3) | 127.4(3) |
| V1–O2–V2         | 108.34(11)        | —       | —    | —    |
| V1–O6–V2         | 110.10(11)        | —       | —    | —    |
| V2–O4–V1         | —                 | 108.68(7) | 109.14(19) | 108.7(2) |
| V1–O8–V2         | —                 | 109.05(7) | 108.65(19) | 108.3(2) |
| V1–N1–C70        | 173.7(3)          | —       | —    | —    |
| V1–N1–C71        | —                 | 176.51(16) | 175.9(5) | —    |
| V2–N2–C81        | —                 | 178.53(17) | 174.3(5) | —    |
| V1–N2–C76A       | —                 | —       | —    | —    |

![Fig. 2 View of the molecular structure of [VO]L1 (2·6MeCN) (H atoms and free MeCN molecules are omitted for clarity; symmetry codes: #1: 1 - x, 1 - y, 1 - z). Selected bond lengths V1–O1 1.8128(14), V1–O2 2.3732(14), V1–O3 2.0152(13), V1–O5 1.5866(15), V1–O6 2.0667(14), V1–O8 1.7869(14), V2–O3 1.9977(13), V2–O4 1.7934(14), V2–O6 1.9822(14), V2–O7 1.5830(15), O5–V1–O8 99.86(7), O5–V1–O1 100.97(7), O8–V1–O1 102.34(6), O5–V1–O3 101.19(7), O8–V1–O5 89.29(6), O1–V1–O3 152.74(6), O5–V1–O6 95.07(7), O8–V1–O6 157.22(6), O1–V1–O6 91.50(6), O3–V1–O6 70.89(5), O5–V1–O2 177.99(6), V2–O3–V1 107.25(6).](Image 341x623 to 518x735)
The molecular structure of 8, as determined using synchrotron radiation, is shown in Fig. 5, with selected bond lengths and angles given in the caption. The molecule sits on a centre of symmetry. Interestingly, the dioxacalix[6]arene has been split in two by a reaction of the bridging oxygen and the p-tolylimido groups. The result is a metallo-macrocycle containing two square-based pyramidal vanadyl centres. The vanadyl V=O4 bond length is typical at 1.5933(4) Å,\(^\text{10}\) whilst the phenoxide bond lengths at 1.8891(15) and 1.9046(15) Å are comparable with those observed elsewhere in vanadyl calixarene chemistry.\(^\text{7,10}\) The two uncoordinated phenolic OH groups are involved in H-bonding to vanadium-bound phenoxide groups. There are four solvent molecules (MeCN) of crystallization per molecule, with two residing inside the metallo-macrocycle. We note that calixarene cleavage is rare, with previous reports involving cleavage of a methylene metallo-macrocycle. We note that calixarene cleavage is rare, with previous reports involving cleavage of a methylene group. The result is a metallo-macrocycle that is a metallo-macrocycle.

### Ring opening polymerization studies

**General:** The performance of these complexes to act as catalysts for the ring opening polymerization (ROP) of ε-caprolactone (ε-CL) (Table S1, ESIf), δ-valerolactone (δ-VL) (Table S2, ESIf), both with and without one equivalent of benzyl alcohol (BnOH) per vanadium present, has been investigated.

Results in the absence of BnOH were less controlled but for completion are presented in the ESIf (Tables S1 and S2). The co-polymerization of ε-caprolactone and δ-valerolactone (Table 4) has also been investigated. In each case, performances are compared against the known complexes I–IV (Chart 2).

**ε-Caprolactone (ε-CL)**

Complexes 1–8 and I–IV were screened for their ability to polymerise ε-caprolactone and the results are collated in Table 2. The polymerization screening indicated that the best conditions were 500 equivalents of ε-caprolactone to vanadium at 130 °C. The activity of complex 1 increased with temperature and peaked at 500 equivalents of monomer. Complex 1 was also active at low catalyst loading leading to 82.5% conversion after 8 h for 1000 equivalents of monomer.

The observed activity of complex 1 surpassed that of the other complexes screened herein, and this was attributed to the additional presence of the sodium centres.

All polymers obtained were of low polydispersity (PDI < 1.6), which suggested that these polymerizations occurred without significant side reactions. Interestingly, only low molecular weight polymers were obtained using these oxovanadium/imido vanadyl systems.

The screening of complexes 1–8 and I–IV (Table 2) revealed that the vanadium-based I\(^\text{1}\) or L\(^\text{2}\)-containing complexes namely 1, 5, 6 and 8 herein, exhibited higher activities than the known complexes I–IV under the conditions employed. After 24 h (Table 1), complexes 2, I, II, III, IV afforded relatively lower conversions (<90%), whereas higher conversions (>90%) were reached using complexes 1, 3–7, 8, under similar conditions. From a kinetic study (Fig. 6a), it was observed that the PCL polymerization rate followed the order: 1 > 8 > II > I > III > 3 > 2 > IV. For complexes within the imido-alkoxide family, the kinetic and TON/TOF results (Table 2, Fig. 6b) showed that the catalytic activity followed the order: 5 (CF\(_3\)) > 6 (Cl) > 7 (F) > 4 (OME) > 3 (Me), which suggested that the presence of electron withdrawing para substituents favours higher activity. \(^1\)H NMR spectra of the PCL indicated the presence of an BnO end group (e.g. Fig. S11, ESIf), which agrees with the MALDI-ToF mass spectra (e.g. Fig. S6, ESIf) and indicates that the polymerization proceeded via a coordination insertion mechanism. The observed molecular weights were lower than the calculated values, whilst the MALDI-ToF mass spectra were consistent with BnO end groups \([M = n \times 114.12 \text{ (CL) + 108.05 (BnOH) + 22.99 \text{ (Na\textsuperscript{+})}}]\).

In the absence of BnOH, spectra (Fig. S5 and S10, ESIf) indicated the products were catenulate with chains and cyclic polymers present. In the MALDI-ToF mass spectra, a part family of peaks consistent with the chain polymer (terminated by 2 OH) \([M = 17 \text{ (OH)} + 1\text{[H] + n \times 114.14 \text{ (CL) + 22.99 \text{ (Na\textsuperscript{+})}}}]\) and the cyclic polymer \([M = 22.99 \text{ (Na\textsuperscript{+})} + n \times 114.14 \text{ (CL)}] \) were observed.

**δ-Valerolactone (δ-VL)**

Complexes 1–8 and I–IV were also evaluated as catalysts in the presence of one equivalent of BnOH for the ROP of

\[\text{CH}_3\text{C}_6\text{H}_4\text{NCH})\text{-4-}\text{Bu-C}_6\text{H}_2\text{O-6-CH}_2\text{-4-}\text{BuC}_6\text{H}_4\text{OH}.\] The molecular structure of 8, as determined using synchrotron radiation, is shown in Fig. 5, with selected bond lengths and angles given in the caption. The molecule sits on a centre of symmetry. Interestingly, the dioxacalix[6]arene has been split in two by a reaction of the bridging oxygen and the p-tolylimido groups. The result is a metallo-macrocycle containing two square-based pyramidal vanadyl centres. The vanadyl V=O4 bond length is typical at 1.5933(4) Å,\(^\text{10}\) whilst the phenoxide bond lengths at 1.8891(15) and 1.9046(15) Å are comparable with those observed elsewhere in vanadyl calixarene chemistry.\(^\text{7,10}\) The two uncoordinated phenolic OH groups are involved in H-bonding to vanadium-bound phenoxide groups. There are four solvent molecules (MeCN) of crystallization per molecule, with two residing inside the metallo-macrocycle. We note that calixarene cleavage is rare, with previous reports involving cleavage of a methylene bridge under acidic conditions.\(^\text{18}\)

**Fig. 5** View of the molecular structure of [VO(L\(^\text{2}\))]\(_2\)-4MeCN (8-4MeCN) (H atoms and MeCN molecules are omitted for clarity) (L\(^\text{2}\) = 2-(p-CH\(_3\)-C\(_6\)H\(_4\)NCH)\text{-4-}Bu-C\(_6\)H\(_2\)O-6-CH\(_2\)-4-BuC\(_6\)H\(_4\)OH). Selected bond lengths (Å) and angles (°): V1–O1 1.9046(15), V1–O3A 1.8891(15), V1–O4 1.5933(17), V1–N1 2.1192(18), V1–N2A 2.1118(19), V1–O1–C9 131.18(14), V1–O3–C31 131.67(13), V1–N1–C1 117.87(19), V1–N1–C(8) 124.00(15).

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δ-VL (Table 3). Using compound 1, the conditions of temperature and [V]: [δ-VL] were varied. Best observed results were achieved at 130 °C using [V]: [δ-VL] at 1:500 over 8 h. As in the case of the ROP of ε-CL, kinetic studies (Fig. 7 and S3, ESI†) revealed that the catalytic activities followed the order: 1 > 8 > II > I > III ≈ 3 > 2 > IV,
whilst the performance of the vanadium-based imido catalysts exhibited the order 5 > 6 ≈ 7 > 4 > 3, which was again suggestive of a positive influence exerted by electron-withdrawing para substituents on the imido group. As for the ROP of ε-CL, there was evidence of significant transesterification and nearly all observed $M_n$ values were significantly lower than the calculated values. The MALDI-ToF mass spectra (Fig. S8, ESI†) exhibited a major family of peaks consistent with OBn end groups [$M = 108.05$ (BnOH) + $n \times 100.12$ (VL) + 22.99 (Na⁺)], and a minor family assigned to cyclic PVL. $^1$H NMR spectra of the PVL also indicated the presence of an BnO end group (e.g. Fig. S13, Table 4).

### Table 4 ROP of co-polymer (ε-CL + δ-VL) using 1-8 and I-IV in the presence of BnOH

| Run | Cat | CL : VL : V : BnOH | $T/°$C | CL : VL | Conv<sup>b</sup> (%) | $M_n$<sub>GPC</sub> × 10<sup>3c</sup> | $M_w$ × 10<sup>3c</sup> | PDI<sup>d</sup> |
|-----|-----|-------------------|--------|---------|-----------------|-----------------|----------------|-------------|
| 1   | 1<sup>e</sup> | 250 : 250 : 1 : 1 | 130 | 45 : 55 | 72.6 | 12.16 | 22.37 | 1.84 |
| 2   | 2<sup>e</sup> | 250 : 250 : 1 : 1 | 130 | 45 : 55 | 75.3 | 1.32 | 2.31 | 1.75 |
| 3   | 3<sup>e</sup> | 250 : 250 : 1 : 1 | 130 | 40 : 60 | 45.2 | 6.68 | 6.23 | 1.33 |
| 4   | 4<sup>e</sup> | 250 : 250 : 1 : 1 | 130 | 33 : 67 | 47.5 | 5.29 | 6.88 | 1.30 |
| 5   | 5<sup>e</sup> | 250 : 250 : 1 : 1 | 130 | 40 : 60 | 59.5 | 7.21 | 8.45 | 1.17 |
| 6   | 5<sup>f</sup> | 250 : 250 : 1 : 1 | 130 | 66 : 34 | 63.7 | 7.44 | 8.95 | 1.20 |
| 7   | 5<sup>g</sup> | 250 : 250 : 1 : 1 | 130 | 66 : 34 | 63.7 | 7.44 | 8.95 | 1.20 |
| 8   | 5<sup>s</sup> | 250 : 250 : 1 : 1 | 130 | 40 : 60 | 57.9 | 6.01 | 7.52 | 1.25 |
| 9   | 6<sup>e</sup> | 250 : 250 : 1 : 1 | 130 | 62 : 38 | 55.4 | 6.21 | 7.69 | 1.24 |
| 10  | 6<sup>f</sup> | 250 : 250 : 1 : 1 | 130 | 50 : 50 | 58.4 | 6.12 | 7.14 | 1.17 |
| 11  | 6<sup>g</sup> | 250 : 250 : 1 : 1 | 130 | 51 : 49 | 60.8 | 6.85 | 8.69 | 1.27 |
| 12  | 7<sup>e</sup> | 250 : 250 : 1 : 1 | 130 | 46 : 54 | 61.1 | 6.95 | 8.69 | 1.25 |
| 13  | 7<sup>f</sup> | 250 : 250 : 1 : 1 | 130 | 40 : 60 | 59.5 | 7.21 | 8.95 | 1.20 |
| 14  | 7<sup>g</sup> | 250 : 250 : 1 : 1 | 130 | 35 : 65 | 49.5 | 4.53 | 7.21 | 1.59 |
| 15  | 8<sup>e</sup> | 250 : 250 : 1 : 1 | 130 | 40 : 60 | 49.5 | 4.53 | 7.21 | 1.59 |
| 16  | 8<sup>f</sup> | 250 : 250 : 1 : 1 | 130 | 35 : 65 | 49.5 | 4.53 | 7.21 | 1.59 |
| 17  | 8<sup>g</sup> | 250 : 250 : 1 : 1 | 130 | 35 : 65 | 49.5 | 4.53 | 7.21 | 1.59 |
| 18  | 9<sup>e</sup> | 250 : 250 : 1 : 1 | 130 | 40 : 60 | 49.5 | 4.53 | 7.21 | 1.59 |

<sup>a</sup> Ratio of ε-CL to δ-VL observed in the co-polymer by $^1$H NMR spectroscopy.  
<sup>b</sup> Determined by $^1$H NMR spectroscopy.  
<sup>c</sup> $M_n$<sub>GPC</sub> values corrected considering Mark–Houwink method from polystyrene standards in THF, $M_n$<sub>GPC</sub> = [0.56 × $M_n$<sub>measured</sub> measured × (1% CL) + 0.57 × $M_n$<sub>measured</sub> measured × (1% VL)] × 10<sup>3</sup>.  
<sup>d</sup> From GPC.  
<sup>e</sup> ε-Caprolactone was firstly added for 24 h, then δ-valerolactone was added and heating for 24 h.  
<sup>f</sup> δ-Valerolactone was firstly added for 24 h, then ε-caprolactone was added and heating for 24 h.  
<sup>g</sup> ε-Caprolactone and δ-valerolactone were added at the same time and heating for 24 h.

**Fig. 6** (a) Relationship between conversion and time for the polymerization of ε-CL by using complex 1–3, 8, and I–IV; (b) relationship between conversion and time for the polymerization of ε-CL by using complexes 3–7; conditions: $T = 130°$C, $n_{Monomer} : n_V : BnOH = 500 : 1 : 1$.

**Fig. 7** (a) Relationship between conversion and time for the polymerization of δ-VL by using 1–3, 8, and I–IV; (b) Relationship between conversion and time for the polymerization of δ-VL by using complexes 3–7; conditions: $T = 130°$C, $n_{Monomer} : n_V : BnOH = 500 : 1 : 1$. 
ESI†). In the absence of BnOH, spectra (Fig. S7 and S12, ESI†) again indicated the products were catenulate. The MALDI-ToF mass spectra exhibited the peaks consistent with the chain polymer (terminated by 2 OH) \([M = 17 (OH) + 1(H) + n \times 100.12 (VL) + 22.99 (Na^+)\] and cyclic polymer \([M = 22.99 (Na^+) + n \times 100.12 (VL)]\).

Kinetics

The kinetic results are consistent with a zero-order dependence in monomer. Whilst this kind of behaviour is uncommon, systems that behave in a similar manner have been reported.\(^{19}\) The dependence of the \(M_n\) and molecular weight distribution on the monomer conversion in the reactions catalyzed by 1, 3 and 8 with BnOH was also investigated (Fig. 8). For the ROP of \(\varepsilon\)-CL, the \(M_n\) was shown to increase linearly with the conversion, which suggested that the polymerization was well controlled (Fig. 8, left). A similar outcome was also observed in the reaction involving \(\delta\)-VL (Fig. 8, right).

Co-polymerization of \(\varepsilon\)-CL and \(\delta\)-VL

The complexes exhibited moderate conversions, with the mixed-metal complex 1 performing best (72.6%), with 5 (\(p\)-CF\(_3\)) and the known complex 1 also producing conversions >60%. Under the conditions employed, the systems 5, 6, 7 and 8 showed a preference for CL incorporation (50–66%), and in the case of 5 and 6, this was despite the initial addition of \(\delta\)-VL. Complex 4 exhibited the highest preference (67%) for VL incorporation. In general, the systems appeared to be relatively well behaved with PDIs in the range 1.17–1.84; NMR spectra were consistent with the presence of BnO and OH end groups (Fig. S15, ESI†). The composition of the copolymer was further investigated by \(^{13}\)C NMR spectroscopy. In fact, diagnostic resonances belonging to CL–VL, CL–CL, VL–VL and VL–CL dyads can be observed in the region between \(\delta\) 63.91 and 64.13 ppm (Fig. 16, ESI†). Based on the current results, the number-average sequence length was found to be 7.16 and 5.30 for CL and VL, respectively, consistent with a randomness degree \(R\) of 0.33, which suggests the copolymers possess a “blocking” tendency (Fig. S16, eqn (S1)–(S3), ESI†).\(^{20}\)

ROP of \(\tau\)-lactide

To enhance the thermal properties of the polymers obtained herein, we also investigated the ROP of the \(\tau\)-lactide. Unfortunately, none of the systems herein proved to be effective as catalysts for the ROP of \(\tau\)-lactide either in solution at high temperatures (130 °C) or as melts.

Ethylene polymerization

The imido complexes 3–7 were screened for their ability to polymerize ethylene in the presence of the co-catalysts R\(_2\)AlCl (R = Me, Et) and the re-activator ethyltrichloroacetate (ETA), see Table 5, showing much higher polymerization activities if Me\(_2\)AlCl was used as activator (cf. entries 1 and 2 of Table 5). In the presence of Me\(_2\)AlCl+ETA, the catalytic activities followed the trend \(3 (p\text{-Me}) \approx 5 (p\text{-CF}_3) > 6 (p\text{-F}) > 7 (p\text{-OMe})\). Complexes 3–7 exhibited high ethylene consumption rates during 10–20 min of polymerization and virtually lost the activity after 30 min (Fig. 9a). Complex 4 showed the lowest reactivity toward ethylene in the series, which may be explained by the presence of strong electron-donating OMe substituents, reducing its electrophilicity. All systems except 4 were relatively well-controlled with PDIs < 2.5 (Fig. 9b) and afforded highly linear (according to \(^{13}\)C NMR spectroscopy, there were no detectable branches, Fig S25, ESI†) high molecular weight polyethylene. The ethylene polymerization activities found here for complexes 3–7, are very high, several times higher than those reported for vanadium polyphenolate and phenoxime catalysts under comparable conditions.\(^{21}\)

Conclusions

In conclusion, the use of \(p\text{-tert}\)-butyltetramidooxacalix[6]arene\(_6\), \(L^\circ\)\(_6\), with [NaVO(OBu)] or [VO(O\(\text{OniPr}\))] affords the mixed-metal complex \([[\text{VO}]_2(\mu\text{-O})\text{Na}_2(L^1)(\text{MeCN})_4]]\) or the tetranuclear complex \([[\text{VO}]_4L^1]]\), respectively. Use of imidoalkoxide precursors \([\text{V}(\mu\text{-O})\text{Na}_2(L^1)]\) leads to the formation of \([[\text{V}(\mu\text{-O})\text{Na}_2(L^1)]\]) type complexes. Under the conditions employed, the calixarene ring system can break in situ, and result in two \(2\text{-}(p\text{-CH}_3\text{C}_6\text{H}_4\text{NCH})4\text{-BuC}_6\text{H}_4\text{O}_6\text{-CH}_2\text{-4-BuC}_6\text{H}_4\text{OH}(L^2)\), which can bind to the vanadium to form a metallocyclic complex of the form \([[\text{VO}(L^2)]]\). All

**Fig. 8** Left: \(M_n\) vs. monomer conversion in the ROP of \(\varepsilon\)-CL by using 1, 3 and 8; right: \(M_n\) vs. monomer conversion in the ROP of \(\delta\)-VL by using 1, 3 and 8; conditions: \(T = 130 ^\circ\)C, nMonomer: \(n_\varepsilon\): BnOH = 500:1:1.
complexes were active for the ROP of the cyclic esters ε-CL and δ-VL, with and without benzyl alcohol (BnOH) present, but not for r-LA. The co-polymerization of ε-CL with δ-VL was also possible. Low molecular weight products were obtained (related oxacalix[3]arene species (less evident. Observed conversion rates were superior to δ substituents favour higher activity, and a similar order for para suggested that the presence of electron withdrawing imido complexes in ROP. For ethylene polymerization (with DMAC/ETA), the large flexibility of the dioxacalix[6]arene scaffold is beneficial under similar conditions. This suggests the presence and large flexibility of the dioxacalix[6]arene scaffold is beneficial in ROP. For ethylene polymerization (with DMAC/ETA), the imido complexes 3 and 5–7 showed very high catalytic activities of the order 0.9–1.5 × 10^{19} g PE (mol V)^{-1} bar^{-1} h^{-1}, which followed the trend 3 (p-Me) ≈ 5 (p-CF3) > 7 (p-F) > 6 (p-Cl), whilst the activity of 4 (p-OME) was much lower and was thought to be due to its reduced electropilicity. The product in each case was highly linear polyethylene.

**Experimental**

**General**

The known compounds L^1 H_6, L^1 H_3, [V(Np-RC_6H_4)(OOr)]_2 (R= OMe, CF_3, Cl), [V(Np-CH_3C_6H_4)(OOr)]_2 and [V(ε-CH_3C_6H_4)(Or)] are α,β-unsaturated carboxylic acid derivatives. 3,5-Dicyanovinyl-2,4-hexadiene was prepared following the procedure described in the literature methods. 7,9,15,16,22 All reactions were conducted under an inert atmosphere using standard Schlenk techniques. Toluene was dried from sodium, acetonitrile was distilled from calcium hydride, diethylether was distilled from sodium benzophenone, and all solvents were degassed prior to use. IR spectra (nujol mulls, KBr or NaCl windows) were recorded on a Nicolet Avatar 360 FT IR spectrometer.

^1H NMR spectra were recorded at room temperature on a Varian VXR 400 S spectrometer at 400 MHz or a Gemini 300 NMR spectrometer or a Bruker Avance DPX-300 spectrometer at 300 MHz. ^1H and ^13C NMR spectra of polyethylene samples (1,2-dichlorobenzene, 100 °C) were recorded on a Bruker Avance 400 MHz NMR spectrometer at 400.130 and 100.613 MHz, respectively. ^1H NMR spectra were calibrated against the residual protio impurity of the deuterated solvent.

Crystal structures were determined from data collected at the UK National Crystallography Service (1–6) and the SRS at Daresbury (8). Full details are given in the ESI. Crystal data are summarised in Table 6.

Elemental analyses were performed by the elemental analysis service at the University of Hull. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry was performed in a Bruker autoflex III smart mass spectrometer.

**Table 5** Ethylene polymerization data for homogeneous catalysts (R-Ph-LV2 + Me2AlCl + ETA)

| Run | Cat | V loading/μmol | Co-catalyst | PE yield/g | Activity^a | M_0 × 10^{-3} | M_w × 10^{-3} | M_w/M_0 | PDI^b |
|-----|-----|----------------|-------------|------------|------------|-------------|-------------|----------|-------|
| 1   | 3   | 1.0           | Et2AlCl     | 0.7        | 1.4        | 110         | 245         | 1.8      | 2.2   |
| 2   | 3   | 0.5           | Me2AlCl     | 7.4        | 14.8       | 72          | 520         | 5.0      | 7.2   |
| 3   | 4   | 0.5           | Me2AlCl     | 1.2        | 2.4        | 74          | 180         | 2.1      | 2.4   |
| 4   | 5   | 0.5           | Me2AlCl     | 7.2        | 14.2       | 74          | 180         | 2.1      | 2.4   |
| 5   | 6   | 0.5           | Me2AlCl     | 4.5        | 9.0        | 120         | 290         | 1.9      | 2.4   |
| 6   | 7   | 0.5           | Me2AlCl     | 6.7        | 13.4       | 74          | 185         | 2.0      | 2.5   |

^a In 10^{19} g PE mol V^{-1} bar^{-1} h^{-1}. ^b PDI = M_w/M_0.

Fig. 9 (a) Activity vs. time plot for entries 4–6 of Table 5. (b) GPC traces of polyethylenes in entries 2 and 4–6 of Table 5.
ambient temperature and then the volatiles were removed.

To a solution of [(VO)₄L₁] (2.02 g, 0.49 mmol) and L₁H₆ (0.50 g, 0.49 mmol) in toluene (20 mL) was added 1H₆ (0.50 g, 0.49 mmol) and the mixture was heated at 0 °C for 12 h. The system was then cooled to room temperature, the volatiles were removed, and the residue was extracted into warm MeCN (20 mL). Prolonged standing at 0 °C afforded a deep brown solid. The product was purified by recrystallization from toluene/hexane (1:1) to afford 4-5 MeCN as orange/red prisms. Single orange prisms were grown from a saturated MeCN (30 mL) solution at 0 °C; yield 0.43 g, 50%. IR (nujol mull, KBr): 3237 w, 1613 w, 1554 w, 1540 w, 1486 m, 1456, 1383, 1362, 1297, 1260, 1206, 1159 m, 1075, 1023, 910, 872, 800s, 754w, 688w. ¹¹B NMR (CDCl₃) δ = 6.87–7.54 ppm. Mass spec (EI): 1470 [M + Na]+.

Synthesis of [(VO₂L₁)₂L₁] (4-MeCN)

As for 2, but using [V(Np-OMe)₂(C₆H₄)L₁] (0.35 g, 1.0 mmol) and L₁H₆ (0.50 g, 0.49 mmol) affording 4-MeCN as orange/red prisms. Single orange prisms were grown from a saturated MeCN (30 mL) solution at 0 °C; yield 0.94 g, 50%. IR (nujol mull, KBr): 3237 w, 1613, 1585m, 1554w, 1456, 1486m, 1383, 1362, 1297, 1260, 1206, 1159 m, 1075, 1023, 910, 872, 800s, 754w, 688. ¹¹B NMR (CDCl₃) δ = 6.87–7.54 ppm. Mass spec (EI): 1470 [M + Na]+.

Preparation of [(VO₄L₁)₂(L₁)][MeCN]₅•MeCN (1:5 MeCN)

To a solution of [(VO₄L₁)₂(L₁)] (2.02 g, 0.49 mmol) and L₁H₆ (0.50 g, 0.49 mmol) in toluene (20 mL) was added 1H₆ (0.50 g, 0.49 mmol) and the mixture was heated at 0 °C for 12 h. The system was then cooled to room temperature, the volatiles were removed, and the residue was extracted into warm MeCN (20 mL). Prolonged standing at 0 °C afforded a deep brown solid. The product was purified by recrystallization from toluene/hexane (1:1) to afford 4-5 MeCN as orange/red prisms. Single orange prisms were grown from a saturated MeCN (30 mL) solution at 0 °C; yield 0.43 g, 50%. IR (nujol mull, KBr): 3237 w, 1613 w, 1554 w, 1540 w, 1486 m, 1456, 1383, 1362, 1297, 1260, 1206, 1159 m, 1075, 1023, 910, 872, 800s, 754w, 688. ¹¹B NMR (CDCl₃) δ = 6.87–7.54 ppm. Mass spec (EI): 1470 [M + Na]+.

Preparation of [(VO₂L₁)L₁][MeCN]₅•MeCN (1:5 MeCN)

To a solution of [(VO₂L₁)L₁] (2.02 g, 0.49 mmol) and L₁H₆ (0.50 g, 0.49 mmol) in toluene (20 mL) was added 1H₆ (0.50 g, 0.49 mmol) and the mixture was heated at 0 °C for 12 h. The system was then cooled to room temperature, the volatiles were removed, and the residue was extracted into warm MeCN (20 mL). Prolonged standing at 0 °C afforded a deep brown solid. The product was purified by recrystallization from toluene/hexane (1:1) to afford 4-5 MeCN as orange/red prisms. Single orange prisms were grown from a saturated MeCN (30 mL) solution at 0 °C; yield 0.43 g, 50%. IR (nujol mull, KBr): 3237 w, 1613 w, 1554 w, 1540 w, 1486 m, 1456, 1383, 1362, 1297, 1260, 1206, 1159 m, 1075, 1023, 910, 872, 800s, 754w, 688. ¹¹B NMR (CDCl₃) δ = 6.87–7.54 ppm. Mass spec (EI): 1470 [M + Na]+.
prisms from a saturated MeCN (30 mL) solution at 0 °C (yield 0.35 g, 51%). Anal. cald for C_{96}H_{108}N_{4}O_{8}V_{2}; MeCN C, 69.29; H, 6.89; N, 2.96%. Found C, 67.72; H, 7.43; N, 2.25%. IR (nujol mull, KBr): 2359 m, 1737 w, 1593 m, 1554 m, 1513 m, 1461 s, 1377 m, 1294 m, 1260 m, 1200 m, 1178 s, 1088 w, 822 w, 795 w, 726 w. 

1H NMR (CDCl3): δ: 6.88–7.69 (m, 12H, ary1H), 6.50 (d, J = 10.0 Hz, 4H, –C6H4–Cl), 6.35 (d, J = 10.0 Hz, 4H, –C6H4–Cl), 4.86–5.09 (m, J = 10.0 Hz, 4H, –OCH2–), 4.68 (d, J = 10.0 Hz, 4H, –OCH2–), 3.41–4.53 (m, 4H, –CH2–), 3.67 (d, J = 12.8 Hz, 4H, –CH2–), 1.13–1.35 (m, 54H, C(CH3)3).

31V NMR (CDCl3): δ: −335.3 ppm (ω1/2 120 Hz). Mass spec (El): 1386 [M]+.

**Synthesis of [{V(Np-F-C6H4)3}3L11] (7-MeCN)**

As for 2, but using [{V(Np-F-C6H4)(OnPr)] (0.34 g, 0.99 mmol) and L1H6 (0.50 g, 0.49 mmol) affording 7-MeCN as red/brown crystals from a saturated MeCN (30 mL) solution at 0 °C. Yield: 0.57 g, 86%. Anal. cald for C_{96}H_{108}N_{4}O_{8}V_{2}; MeCN C, 70.92; H, 6.75; N, 3.03%. Found C, 70.72; H, 6.89; N 3.38%. IR (nujol mull, KBr): 2360 w, 2341 w, 1682 w, 1510 m, 1411 w, 1299 w, 1260 s, 1228 m, 1202 s, 1154 w, 1146 s, 1096 w, 1064 w, 1018 s, 988 w, 912 w, 872 w, 832 w, 821 s, 806 s, 722 m, 668 w, 581 w, 460 w. 

1H NMR (CDCl3): δ: 6.84–7.81 (m, 12H, ary1H), 6.49 (d, J = 6.8 Hz, 4H, –NC6H4–Cl), 5.91 (d, J = 6.8 Hz, 4H, –NC6H4–Cl), 4.91–4.98 (d, J = 8.8 Hz, 4H, –OCH2–), 4.49 (d, J = 8.8 Hz, 4H, –OCH2–), 4.13–4.26 (m, 4H, –CH2–), 3.69 (d, J = 5.2 Hz, 4H, –CH2–), 1.36–1.09 (m, 54H, C(CH3)3). 19F NMR (CDCl3): δ: 108.30 ppm. 51V NMR (CDCl3): δ: −173.4 ppm (ω1/2 265 Hz).

**Synthesis of [VO(L1)]2 (L1 = 2-((p-tolylNCH)-4-Bu-C6H4-O-6-CH2)-4-Bu-C6H4-OH) (8-MeCN)**

[V(Np-tolyl)(OEt)] (0.29 g, 0.99 mmol) and L1H6 (0.50 g, 0.49 mmol) were refluxed in toluene (30 mL) for 12 h. Following removal of volatiles in vacuo, the residue was dissolved in hot MeCN (30 mL), filtered and left to stand (1–2 days) at 0 °C to afford 8 as orange-brown prisms (0.43 g, 29% yield). Anal. cald for C_{96}H_{108}N_{4}O_{8}V_{2}; MeCN C, 74.49; H, 7.03; N 3.62%; found C, 73.60; H, 7.12; N, 2.88%. IR (nujol mull, KBr): 3231 w, 1613 m, 1593 m, 1555 w, 1505 w, 1459 s, 1377 s, 1363 m, 1299 w, 1261 s, 1209 s, 1073 s, 1018 s, 991 s, 965 s, 878 s, 871 s, 839 m, 818 m, 802 s, 765 w, 764 m, 753 m, 737 m. 

1H NMR (CDCl3) results of complex 7. 1H NMR (CDCl3): δ: 7.01 (s, 2H, –OH), 6.84–7.68 (m, 12H, ary1H), 6.45 (d, J = 8.4 Hz, 4H, –NC6H4–Me), 6.16 (d, J = 8.4 Hz, 4H, –NC6H4–Me), 4.85–5.10 (d, J = 9.6 Hz, 4H, –N–CH2–), 4.53–4.65 (d, J = 9.6 Hz, 4H, –N–CH2–), 4.25–4.34 (m, 4H, –CH2–), 3.65 (d, J = 12.8 Hz, 4H, –CH2–), 2.33 (m, 12H, –CH2–), 2.01 (s, 3H, MeCN), 1.11–1.36 (m, 54H, C(CH3)3). 31V NMR (CDCl3) δ: −313.2 ppm (ω1/2 512 Hz). Mass spec (El): 1556 [M + Na]–3MeCN.

**Procedure for ROP of ε-caprolactone/δ-valerolactone**

A toluene solution of pre-catalyst (0.010 mmol, 1.0 mL toluene) was added into a Schlenk tube in the glove-box at room temperature. The solution was stirred for 2 min, and then the appropriate equivalent of BnOH (from a pre-prepared stock solution of 1 mmol BnOH in 100 mL toluene) and the appropriate amount of ε-CL or δ-CL along with 1.5 mL toluene was added to the solution. For example, for Table 2, entry 1, a toluene solution of pre-catalyst 1 (0.010 mmol, 1.0 mL toluene) was added into a Schlenk tube, then 2 mL BnOH solution (1 mmol BnOH/100 mL toluene) and 20 mmol ε-CL along with 1.5 mL toluene was added to the solution. The reaction mixture was then placed into an oil/sand bath pre-heated at 130 °C, and the solution was stirred for the prescribed time (8 or 24 h). The polymerization mixture was quenched on addition of an excess of glacial acetic acid (0.2 mL) into the solution, and the resultant solution was then poured into methanol (200 mL). The resultant polymer was then collected on filter paper and was dried in vacuo.

**Kinetic studies**

The polymerizations were carried out at 130 °C in toluene (2 mL) using 0.010 mmol of complex. The molar ratio of monomer to initiator was fixed at 500:1, and at appropriate time intervals, 0.5 μL aliquots were removed (under N2) and were quenched with wet CDCl3. The percent conversion of monomer to polymer was determined using 1H NMR spectroscopy.

**Procedure for ethylene polymerization**

Ethylene polymerization experiments were performed in a steel 500 mL autoclave. The reactor was evacuated at 80 °C, cooled down to 20 °C and then charged with the freshly prepared solution of the co-catalyst in heptane/toluene. Pre-catalysts were introduced into the reactor in sealed glass ampoules, containing 0.5 or 1.0 μmol of appropriate V-complex in 0.5 mL of solvent. After setting up the desired temperature and ethylene pressure, the reaction was started by breaking the ampoule with the pre-catalyst. During the polymerization, ethylene pressure (2 bar), temperature (70 °C) and stirring speed (2000 rpm) were maintained constant. After 30 min (during which time the ethylene consumption rate declined to nearly zero level), the reactor was opened to the atmosphere and the polymeric product was dried in a fume-hood to a constant weight.

**Polymerization conditions.** For entry 1 of Table 5: V loading 1.0 μmol (dissolved in CH2Cl2), co-catalyst Et2AlCl + ETA (molar ratio V:Et2AlCl: ETA = 1:1000:500) in 50 mL of toluene + 100 mL of heptane, T pol 70 °C, P C2H4 = 2 bar, for 30 min. For entries 2–8 of Table 5: V complex was dissolved in toluene, Co-catalyst Me2AlCl + ETA (molar ratio V:Me2AlCl:ETA = 1:1000:1000) in 100 mL of toluene + 100 mL of heptane, T pol 70 °C, P C2H4 = 2 bar, for 30 min.

**Crystallography**
Table 6  Crystal structure data for 1.5MeCN, 2.6MeCN, 3.7-MeCN-0.5CH2Cl2, 4.4-MeCN, 5, 6, 7, 8.4-MeCN\textsuperscript{a,b} (ref. 24)

| Compound                  | 1.5MeCN  | 2.6MeCN  | 3.7-MeCN-0.5CH2Cl2 | 4.4-MeCN |
|---------------------------|----------|----------|---------------------|----------|
| Formula                   | C_{86}H_{109}N_{9}Na_{2}O_{11}V_{2} | C_{86}H_{114}N_{10}O_{16}V_{4} | C_{155}H_{223}Cl_{2}N_{23}O_{32}V_{8} | C_{96}H_{109}N_{10}O_{19}V_{2} |
| Crystal system            | Triclinic| Triclinic| Triclinic           | Triclinic|
| Space group               | P1       | P1       | P1                  | P1       |
| Unit cell dimensions      |          |          |                     |          |
| a (Å)                     | 13.4214(3)| 12.498(4)| 19.7899(3)          | 14.03537(8) |
| b (Å)                     | 15.454(5)| 15.627(4)| 21.673(3)          | 17.33956(12) |
| c (Å)                     | 25.249(7)| 14.1554(3)| 22.7696(5)         | 20.19059(12) |
| α (°)                     | 85.709(3)| 68.166(2)| 69.271(2)          | 71.1684(6) |
| β (°)                     | 78.946(2)| 79.128(2)| 76.567(2)          | 84.4591(5) |
| γ (°)                     | 69.251(3)| 75.546(2)| 78.6270(10)       | 66.4561(6) |
| V (Å³)                    | 4435.9(2)| 2165.9(10)| 8407.9(3)        | 4260.58(4) |
| Z                          | 2        | 1        | 1                   | 1        |
| Temperature (K)           | 100(2)   | 100(2)   | 100(2)              | 100(2)   |
| Wavelength (Å)            | 0.71103  | 0.51478  | 0.71073             | 1.54178  |
| Calculated density (g cm\(^{-3}\)) | 1.192 | 1.297 | 1.237 | 1.180 |
| Absorption coefficient (mm\(^{-1}\)) | 0.281 | 4.049 | 0.294 | 2.303 |
| Transmission factors (min./max.) | 0.6744 and 1.000 | 0.7111 and 1.000 | 0.7444 and 1.000 | 0.285 and 1.000 |
| Crystal size (mm\(^{3}\)) | 0.14 × 0.07 × 0.01 | 0.16 × 0.07 × 0.035 | 0.06 × 0.06 × 0.02 | 0.18 × 0.08 × 0.035 |
| Number of parameters      | 975      | 518      | 1863                | 970      |
| Reflections measured      | 80640    | 95054    | 110251             | 28571    |
| Unique reflections        | 19896    | 7886     | 38753              | 28571    |
| R_{int}                   | 0.074    | 0.0519   | 0.0626             | 0.057    |
| Reflections with F^2 > 2σ(F^2) | 13237 | 7406 | 24217 | 26256 |
| Largest difference peak and hole (e Å\(^{-3}\)) | 1.37 and −0.69 | 1.009 and −0.489 | 2.04 and −0.87 | 0.61 and −0.43 |
| ɛ                          | 0.11     | 0.18     | 0.12               | 0.22     |

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**Notes:**

- \(^{a}\) Ref. 24. \(^{b}\) For 8: data collected on a Bruker APEX 2 CCD diffractometer at Daresbury SRS station 9.8 (\(\lambda = 0.6710 \text{ Å}\)). ɛ = (β − α)/60.\(^{14}\)
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Conflicts of interest

There are no conflicts to declare.

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