Electronic Supplementary Material

Reaction of Ph₂C(X)(CO₂H) (X = OH, NH₂) with [VO(OR)₃] (R = Et, *n*Pr): Structure, magnetic susceptibility and ROP capability.

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Experimental

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. 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 at room temperature on a Varian VXR 400 S spectrometer at 400 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. The precursors $[VO(OR)_3]$ (R = Et, *n*-Pr) and the pro-ligands dpgH and benzH were purchased from Sigma Aldrich.

Synthesis of $\{VO(OEt)(\mu-OEt)[Ph_2C(NH_2)(CO_2)]\}_2$ (1)

To 2,2'-diphenylglycine (1.00 g, 4.40 mmol) in toluene (20 mL) was added [VO(OEt)₃] (1.60 mL, 8.80 mmol) and the system was refluxed for 12 h. On cooling, the volatiles were removed *in vacuo*, and the residue was extracted into hot MeCN (30 mL). On standing at ambient temperature for 24

h, yellow prisms of 1 formed. Yield 1.15 g, 68 %. $C_{36}H_{44}N_2O_{10}V_2$ requires C 56.40, H 5.79, N 3.66 %. Found C 56.12, H 6.04, N 3.83 %. IR (cm⁻¹): 3292w, 2367w, 3240w, 1669s, 1629m, 1598m, 1588m, 1532w, 1494m, 1462s, 1448s, 1377m, 1364s, 1357s, 1347m, 1302m, 1290m, 1261s, 1221w, 1198m, 1165m, 1143m, 1089s, 1041s, 1022s, 986s, 964w, 932w, 913m, 881m, 813s, 800s, 772w, 761m, 730m, 707m, 696s, 677w, 664w. M.S. 721 (M⁺ – OEt), 708 (M⁺ – 2Et). M.S. (Electrospray in dry MeCN) 748 (M⁺ – H₂O), 539 (M⁺ – Ph₂C(NH₂)(CO₂)H), 523 (M⁺ – Ph₂C(NH₂)(CO₂)H – O). ¹H NMR (CD₃CN) δ : 7.49 – 7.15 (overlapping m, 20H, aryl*H*), 3.49 (q, 8H, *J* = 6.8 Hz, OCH₂), 2.45 (bs, 2H, NH₂), 1.08 (t, 12H, *J* = 6.8 Hz, CH₃); 2x N*H* not observed. ⁵¹V NMR (C₆D₆) δ : –601.1

Synthesis of $\{VO(On-Pr)(\mu-On-Pr)[Ph_2C(NH_2)(CO_2)]\}_2 \cdot 2MeCN (2 \cdot 2MeCN)$

As for 1, but using 2,2'-diphenylglycine (1.00 g, 4.40 mmol) and $[VO(On-Pr)_3]$ (2.00 mL, 8.80 mmol) and cooling to -5 °C affording yellow prisms of **2**·2MeCN. Yield 1.21 g, 61%. C₄₀H₅₂N₂O₁₀V₂ (dried *in vacuo* for 2 h, -2MeCN) requires C 58.39, H 6.37, N 3.41%. Found C 58.98, H 6.95, N 2.44%. IR (cm⁻¹): 3344w, 3301w, 3268w, 3242w, 2349w, 1671s, 1592w, 1582w, 1565w, 1492m, 1351w, 1338w, 1261s, 1191s, 1157m, 1122s, 1091s, 1078s, 1057s, 1048s, 1028s, 978s, 952m, 905w, 895w, 860w, 845w, 801s, 772w, 757w, 727w, 705w, 697m, 675w. M.S. (Electrospray in dry MeCN) 787 (M⁺ – 2MeCN – 2H₂O), 684 (M⁺ – 2*n*Pr – O*n*Pr). ¹H NMR (CD₃CN) δ : 7.81 – 6.96 (3x overlapping m, 20H, aryl*H*), 4.85 (t, *J* = 6.8 Hz, 4H, OCH₂), 3.40 (t, *J* = 6.8 Hz, 4H, OCH₂), 1.74 (m, *J* 6.8 Hz, 4H, OCH₂CH₂), 1.44 (m, *J* = 6.8 Hz, 4H, OCH₂CH₂CH₂), 0.94 (t, *J* = 6.8 Hz, 6H, OCH₂CH₂CH₃), 0.87 (t, *J* = 6.8 Hz, 6H, OCH₂CH₂CH₃); NH₂ not observed. ⁵¹V NMR (C₆D₆) δ : –601.2.

Synthesis of $\{V_8(O)_4Na_{0.75}(OEt)_8[Ph_2C(OH)(CO_2)]_{12}\}$ ·8MeCN (**3**·8MeCN)

Benzilic acid (1.00 g, 4.38 mmol) and [VO(OEt)₃] (0.52 mL, 2.9 mmol) were refluxed in toluene (30 mL) for 12h. On cooling, the volatiles were moved *in vacuo*, and following work-up (extraction into MeCN), small red/brown prisms were isolated on standing for several days at 0 °C. Yield: 0.12 g, 8%. $C_{192}H_{188}Na_{0.75}O_{48}V_8$ ·8MeCN requires C 62.19, H 5.32, N 2.79%. Found C 62.04, H 5.42, N 3.12%. IR (cm⁻¹): 2352w, 2336w, 2320w, 1953w, 1887w, 1714w, 1704m, 1694m, 1682m, 1667m, 1660m, 1651m, 1644m, 1634m, 1614m, 1601m, 1574m, 1567m, 1557m, 1538m, 1532m, 1504m, 1494m, 1316m, 1261s, 1219m, 1156m, 1093s, 1019s, 940m, 918m, 889m, 873m, 801s, 726m, 695m, 667w, 638w. M.S. (nano-electrospray, cone 20V): 2928 (M⁺ – 8MeCN – 2benz – 5OEt – 4O – Na_{0.75}).

Synthesis of {V₈(O)₄Na_{0.74}(OEt)₈[Ph₂C(OH)(CO₂)]₁₂}·3.75MeCN (4·3.75MeCN)

Benzilic acid (1.00 g, 4.38 mmol), NaI (0.06 g, 0.4 mmol) and $[VO(OEt)_3]$ (0.52 mL, 2.9 mmol) were refluxed in toluene (30 mL) for 12 h. On cooling, the volatiles were moved *in vacuo*, and following work-up (extraction into MeCN), red/brown prisms were isolated on standing for several days at 0 °C. Yield: 0.41 g, 24%. C₁₈₄H₁₇₂Na_{0.74}O₄₈V₈·9MeCN* requires C 61.49, H 5.08, N 3.19%. Found C 62.81, H 5.31, N 3.06%. IR (cm⁻¹): 2357w, 2336w, 1659m, 1575s, 1489m, 1403s, 1318m, 1277m, 1261s, 1209w, 1169m, 1158m, 1094s, 1029s, 941w, 918m, 895m, 803s, 764m, 721m, 669s, 676w, 638m. M.S. (MALDI-ToF): 3608 (MH⁺– 3.75MeCN).

* The sample recrystallized from acetonitrile for elemental analysis contained 9MeCN and this was the best analysis we obtained.

Synthesis of {V₈(O)₄Na_{0.45}(OnPr)₈[Ph₂C(OH)(CO₂)]₁₂}·6.38MeCN (5·6.38MeCN)

As for **3**, but using benzilic acid (1.00 g, 4.38 mmol), NaH (0.01 g, 0.4 mmol) and [VO(O*n*Pr)₃] (0.67 mL, 3.0 mmol) affording red/brown prisms of **5**·6.38MeCN. Yield: 0.41 g, 28 %. C₁₉₂H₁₈₈Na_{0.45}O₄₈V₈·6.38MeCN requires C 62.36, H 5.29, N 2.27%. Found C 62.64, H 5.46, N 3.22 %. IR (cm⁻¹): 2351w, 2318w, 1747w, 1738w, 1732w, 1722w, 1714w, 1693w, 1688m, 1667s, 1614m, 1600m, 1580w, 1568w, 1317m, 1306m, 1276s, 1261s, 1207w, 1150m, 1096s, 1018s, 1 940m, 918m, 889w, 872m, 801s, 760m, 722s, 699s, 666w, 639m. M.S. (MALDI-ToF): 3944 (MH⁺), 3713 (MH⁺ – 5.38MeCN – 0.45Na).

Synthesis of $\{V_8(O)_4Na_{0.77}(OnPr)_8[Ph_2C(OH)(CO_2)]_{12}\}$ ·4(MeCN) (6·4MeCN)

As for 3, but using benzilic acid (1.00 g, 4.38 mmol), NaI (0.06 g, 0.4 mmol) and [VO(O*n*Pr)₃] (0.67 mL, 3.0 mmol) affording red/brown prisms of 6·4MeCN. Yield: 0.38 g, 27%. C₁₉₂H₁₈₈Na_{0.77}O₄₈V₈·4MeCN requires C 59.85, H 4.92, N 1.45%. Found C 58.93, H 4.68, N 1.03%. IR (cm⁻¹): 2351w, 2319w, 1748w, 1732w, 1722w, 1715w, 1704w, 1698w, 1694w, 1688m, 1667m, 1660m, 1651m, 1644m, 1633m, 1621s, 1614s, 1580s, 1574s, 1568s, 1539m, 1520w, 1398s, 1318m, 1260s, 1168m, 1094s, 1045s, 1018s, 941w, 916w, 889w, 874w, 801s, 721m, 699s, 675w, 666w, 638w. M.S. (MALDI-ToF): 3577 (MH⁺ – 4MeCN – 0.77Na – O*n*Pr – *n*Pr).

Synthesis of $\{V_8(O)_4K_{0.20}(OnPr)_8[Ph_2C(OH)(CO_2)]_{12}\}$ ·7(MeCN) (7·7MeCN)

As for **3**, but using benzilic acid (1.00 g, 4.38 mmol), KH (0.01 g, 0.3 mmol) and [VO(O*n*Pr)₃] (0.67 mL, 3.0 mmol) affording red/brown prisms of 7·7MeCN. Yield: 0.48 g, 33%. C₁₉₂H₁₈₈K_{0.2}O₄₈V₈·7MeCN requires C 62.38, H 5.31, N 2.47%. Found C 62.39, H 6.00, N 2.30 %. IR (cm⁻¹): 2407w, 2352w, 2335w, 2291w, 2251w, 1956w, 1887w, 1815w, 1666m, 1651s, 1645m, 1634m, 1580s, 1574s, 1563s, 1519m, 1470s, 1446s, 1317s, 1276s, 1260s, 1221m, 1172m, 1089m, 1030s, 1016s, 940s, 918s, 893s, 806s, 780s, 761s, 727s, 699s, 667w, 638m. M.S. (MALDI-ToF): 3713 (MH⁺ – 6MeCN – 0.2K), 3603 (MH⁺ – 6MeCN – 2O*n*Pr).

Synthesis of $\{V_8(O)_4K_{0.30}(OnPr)_8[Ph_2C(OH)(CO_2)]_{12}\}$ ·8(MeCN) (8·8MeCN)

As for **3**, but using benzilic acid (1.00 g, 4.38 mmol), KI (0.07 g, 0.42 mmol) and [VO(O*n*Pr)₃] (0.67 mL, 2.95 mmol) affording red/brown prisms of **8**·8MeCN. Yield: 0.44 g, 30%. C₁₉₂H₁₈₈K_{0.3}O₄₈V₈·8MeCN requires C 62.28, H 5.33, N 3.49%. Found C 63.17, H 5.62, N 3.10%. IR (cm⁻¹): 2422w, 2351w, 2335w, 1985w, 1958w, 1927w, 1809w, 1738w, 1715w, 1667s, 1633m, 1615m, 1600s, 1579m, 1538w, 1505w, 1417w, 1316s, 1277s, 1176s, 1150m, 1092m, 1074s, 1028s, 1000m, 971w, 940s, 918s, 865w, 842w, 808s, 760s, 720s, 700s, 667w, 638s, 611w. M.S. (MALDI-ToF, sample dried *in vacuo* for 15 min. – MeCN): 3725 (MH⁺ – 7MeCN), 3653 (MH⁺ – 7MeCN – 0.3K – *n*PrOH).

X-ray Crystallography

Diffraction data were collected at low temperature either with laboratory-based instrumentation, or synchrotron radiation in the cases of **3**·8MeCN and **7**·7MeCN. Data were corrected for Lorenz and polarization factors and for absorption. Structures were solved by direct methods or dual-space, charge flipping algorithms and refined via full-matrix least-squares.¹⁻³ Further details are provided in the deposited cif files, Table S1, and for each individual structure below. It is worth making some general comments about the V₈ complexes. Structures **3**·8MeCN, **5**·6.38MeCN, **6**·4MeCN, **7**·7MeCN, and **8**·8MeCN are isomorphic and vary only by the nature of the alkali metal, or its occupancy factor, the alkoxide, and the amount of MeCN of crystallization. The precise amount of the latter should be taken as approximate. Some alkoxide R groups were modelled as

disordered, or partially so, and supported with restraints. Difference electron density maps are provided for each of the V_8 structures highlighting the difficulties with this part of the structure in some cases. Each of these has the V8 complex located on a centre of symmetry. The data quality for 6.4MeCN was less good, but the structure in accord with the rest. Structure 4.3.75MeCN is also closely related, with the b axis roughly doubled, and here a whole V_8 complex is unique. In some cases, the MeCN of crystallization was badly disordered, and was then modelled using the Platon Squeeze procedure, in which case the formula includes the squeezed solvent.⁴ Where possible, MeCNs were modelled as point atoms. The OH hydrogens either formed H-bonds with neighbouring coordinated carboxylate oxygens, or pointed the other way and formed H-bonds with MeCNs of crystallization. Given the factional amount of the central alkali metal, and the requirement for charge balance, we assume that there must be some OH hydrogens missing to compensate. It is most likely that this is disordered over most, if not all, of the molecule, so it was essentially impossible to pinpoint where this had occurred. All OH atoms were thus included at full weight but in reality, the amount should be reduced by the amount of alkali metal present. CCDC 2320818-21 (for 1, 2·2MeCN, 3·8MeCN, 4·3.75MeCN) and 2320775-78 (for 8·8MeCN,

5.6.38MeCN, 6.4MeCN, 7.7MeCN) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.



Figure S1. Two views of the molecular structure of **1**. H atoms not involved in H-bonding omitted for clarity.



Figure S2. Packing of 1 viewed parallel to the *c* axis.

For 1: C₃₆H₄₄N₂O₁₀V₂. {VO(OEt)(µ-OEt)[2,2'-(NH₂)(CO₂)CPh₂)]}₂

This is a dimeric V(V) complex on an inversion centre, so half is unique. The vanadium centres are octahedral. Intramolecular NH H-bonding to a terminal ethoxy group is present. There is an

intermolecular N–H···O H-bond to the carbonyl O on a neighbouring molecule. Four intermolecular H-bonds per dimer result in the formation of 2D sheets in the a/b plane. The sheets stack via van der Waals forces in the *c* direction.



Figure S3. H-bonding in the molecules of $2 \cdot 2$ MeCN. H atoms not involved in H-bonding omitted for clarity.



Figure S4. Packing of $2 \cdot 2$ MeCN into 1D chains via the intermolecular H-bonds viewed parallel to *c*.

For 2·2MeCN: $C_{40}H_{52}N_2O_{10}V_2$ ·2(C_2H_3N). {VO(OnPr)(μ -OnPr)[2,2/-(NH₂)(CO_2)CPh₂)]}₂·2MeCN.

There are two half-molecules in the asymmetric unit. The molecule containing V(1) exhibits two intramolecular N–H···O H-bonds, plus two intermolecular H-bonds to MeCN molecules. The molecule containing V(2) shows a different H-bonding pattern. While there are still the N–H···O intramolecular H-bonds, the second N–H links to O(2) in the molecule containing V(1), so the two molecules are H-bonded together forming 1D chains. One unique MeCN is H-bonded to the molecule containing V(1), the other is not H-bonded.



Figure S5. Molecular structure of $\{V_8(O)_4Na_{0.75}(On-Pr)_8[Ph_2C(OH)(CO_2)]_{12}\}$ ·8MeCN (3·8MeCN).



Figure S6. Difference electron density map for 3.8MeCN.

For **3**·8MeCN: Data for this sample was collected at Daresbury Laboratory Station 9.8. $C_{192}H_{188}Na_{0.75}O_{48}V_8 \cdot 8(C_2H_3N)$. $V_8(O)_4Na_{0.75}(On-Pr)_8[Ph_2C(OH)(CO_2)]_{12} \cdot 8(MeCN)$. Half of this is the asymmetric unit. The Na⁺ is partially occupied with refined occupancy 75(3)% and lies on the centre of symmetry. There is some intramolecular H-bonding between OH and carboxylate oxygens. Note this is essentially isostructural with **5**·6.38MeCN (see below), which has the same alkoxide, but a slightly different amount of Na⁺ and solvent of crystallisation. One unique MeCN of crystallisation was modelled as point atoms, but disordered over two sets of positions with major occupancy 58.5(12)%, and thus there are two per V₈ complex. There were also other badly disordered MeCNs. Platon Squeeze recovered 238 electrons over two voids, so 12 MeCNs per cell, or another 6 per V₈ complex making 8 in total. Some geometric and anisotropic displacement parameter restraints were applied. The minor disorder component of the point atom modelled MeCN H-bonds to O(15)–H(15). Other OH hydrogens may form H-bonds to the squeezed MeCNs.



Figure S7. View of the molecular structure of 4.3.75 MeCN.



Figure S8. Difference electron density map for 4.3.75MeCN.

For 4·3.75MeCN: $C_{184}H_{172}Na_{0.74}O_{48}V_8 \cdot 3.75(C_2H_3N)$. $V_8(O)_4Na_{0.74}(OEt)_8(benz)_{12} \cdot 3.75(C_2H_3N)$. This is the asymmetric unit, but the amount of MeCN of crystallisation should be taken as approximate, as Platon detects a small solvent-accessible 'void' which may contain a little more MeCN, but the structure was not 'Squeezed'. In this example, the whole molecule is unique. The Na⁺ ion is partially occupied and disordered over two positions with the two disordered components being 59.4(16) and 15.0(9)%. The Ph ring C(51) > C(56) was modelled as two fold disordered for all atoms except O(28)/O(29)/C(127)/C(128). Initial modelling suggested approximately 50/50 occupancy, so this was fixed at exactly 50/50. The geometry here is not ideal, despite the use of similarity restraints to other, better defined, acid ligands and the situation is complicated by close proximity to a symmetry-related V_8 ring. The Me group on the OEt ligand at O(42) was modelled as split over two sets of positions with major component 59.0(19)%. The Et moiety in the OEt ligand at O(44) was also modelled as two-fold disordered with major component 53.6(17)%. MeCNs at N(1) & N(4) were modelled as split over two sets of positions with major components 64.9(10) and 60.9(19)%, respectively. MeCN at N(2)/N(2X) had disorder components fixed at 0.25 and 0.5, respectively and these are associated with the 50/50 benzilic disorder described previously. OH groups at O(6), O(21), and O(27) form H bonds with MeCN molecules of crystallisation. OH groups at O(3), O(15), O(18), O(21), O(33), & O(36) form intramolecular H-bonds to a carboxylate oxygen in the same ligand forming 5-membered rings.

Figure S9. Core of 5.6.38MeCN. Ph rings and most H atoms omitted for clarity.

Figure S10. Difference electron density map for 5.6.38MeCN.

For **5**.6.38MeCN: $C_{192}H_{188}Na_{0.45}O_{48}V_8$.6.38(C_2H_3N). $V_8(O)_4Na_{0.45}(On-$

 $Pr)_8[Ph_2C(OH)(CO_2)]_{12}$ ·6.38(C₂H₃N). The molecule lies on a centre of symmetry so half is unique. There is evidence of non-merohedral twinning in this structure. TwinROTMAT was tried, however no viable twin law was found. The central Na⁺ ion is modelled as partially occupied 44.9(13)% with the occupancy refined. In all cases the OH H atoms needed to be included in a constrained manner with either rotational freedom or aligned to make the most reliable H-bond. There is twofold disorder present at C(30), O(9), and the phenyl ring C(37) > C(42) which makes up part of the benzilic acid group containing O(7) and O(8). The major occupancy is 56.5(8)%. C(58) and O(15) as well as both phenyl, rings at C(59) > C(64) and C(65) > C(70) of the benzilic acid group at O(13) and (14), are also modelled as two-fold disordered with a major occupancy 69.3(3)%. Additionally, the On-Pr groups containing O(20) and O(21) are also modelled with two-fold order. For the group at O(20) all three of the carbon atoms C(88), C(89), and C(90) have two sets of positions and the major occupancy is 69.4(8)%. For the group at O(21), two-fold disorder is only observed at C(92) and C(93). The major occupancy is 79.1(8)%. There are 1.69 unique MeCNs present that were modelled as point atoms and lie *exo* to the structure, with that at N(2) > C(100) modelled with partial occupancy of 69.3(3)%. This partial occupancy is caused by the proximity with the disordered benzilic acid group at O(13) and O(14) and the occupancy factors are therefore linked. The MeCN N(1) > (C98) is modelled as two-fold disordered with major occupancy 69.3(3)%, again linked with the aforementioned disorder. Platon squeeze recovered 120 electrons in total with 60 in each of two voids. This was interpreted as 3 MeCNs per whole molecule and 6 per cell. This totalled to 6.38 MeCN per molecule. There are some weak C–H… π interactions between the benzilic aryl rings on neighbouring molecules.

Figure S11. View of the asymmetric unit, comprising half a V_8 complex, showing the modelled disorder in 6.4MeCN with minor components having open bonds.

Figure S12. Difference electron density map for 6.4MeCN.

For 6.4 MeCN:	$C_{192}H_{188}Na_{0.77}O_{48}V_8 \cdot 4(C_2H_3N).$	V ₈ (O) ₄ Na _{0.77} (On-
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 $Pr)_8[Ph_2C(OH)(CO_2)]_{12}\cdot4(C_2H_3N)$. The molecule is located on a centre of symmetry so half is unique. Data is of low-quality to a resolution of only 1 Å. The central Na⁺ ion is modelled as partially occupied 77(4)% with the occupancy refined. There may be additional hydrogen bonds to solvent molecules, suggested by H atoms pointing away from the adjacent carboxylate oxygen rather than forming intramolecular H-bonds, however in this case no point atom solvent of crystallisation was refined due to the poor data quality. Two-fold disorder is present at all four of the On-Pr⁻ groups. For the group at O(19), two atoms in the chain C(86) and C(87) are modelled with two positions with a major occupancy of 72.6(19)%. For the additional three On-Pr⁻ groups all three of the carbon positions are modelled as 2-fold disordered. The major occupancies are 53.0(2), 54.2(19), and 65(3)% at O(20), O(21), and O(22), respectively. There is further two-fold disorder present at the benzilic acid group including atoms O(13) and O(14); the whole group is disordered including the joining carbon to the phenyl groups C(58) and the oxygen O(15). The major occupancy is 51.8(8)%. Platon squeeze recovered 177 electrons in total with approximately 88 electrons in each of two voids. MeCN has 22 electrons so 4 in each void or 8 per cell. This totalled to 4 MeCN per V₈ molecule.

Figure S13. Alterative view of 7.7MeCN viewed parallel to the V₈ plane.

Figure S14. Difference electron density map for 7.7MeCN.

For 7.7MeCN: Data for this sample was collected at Daresbury Laboratory, Station 9.8.

 $C_{192}H_{188}K_{0.20}O_{48}V_8 \cdot 7(C_2H_3N). V_8(O)_4K_{0.20}(On-Pr)_8[Ph_2C(OH)(CO_2)]_{12} \cdot 7(C_2H_3N).$

The molecule lies on a centre of symmetry so half is unique. The central K⁺ ion is modelled as partially occupied 19.8(10)% with the occupancy refined. In all cases the OH H atoms needed to be included in a constrained manner with either rotational freedom or aligned to make the most reliable H-bond. Hydrogen bonds are present between N(2) and H(3), O(4) and H(6), N(2) and H(9), N(1X) and H(12), N(1X) and H(15) & O(17) and H(18). N(1X) is the minor occupied site and as such hydrogen bonds between N(1X) and H(12) & N(1X) and H(15) only occur when the solvent is present at the minor site. The 8 V atoms all lie in one plane as do the cores of 4 benzilic acid derived molecules where a single acid bridges a pair of V atoms. Where two benzylic acid

molecules bridge a pair of V atoms, these lie one above and one below the V₈ plane. The On-Pr ligands all point out of the plane, with one up and one down as they bridge pairs of V atoms in pairs at the bridge where there is only one benzilic acid. Where there are two benzilic acid derived ligands bridging pairs of V atoms there is also an oxo group that additionally binds to the partiallyoccupied central K⁺ ion. 8 MeCN molecules per unit cell (4 per V₈ complex) were modelled with the Platon Squeeze procedure. These were badly disordered. Squeeze recovered 207 electrons per unit cell in two large voids with 100 electrons in each, so 4 MeCNs in each void. 1.5 unique MeCN molecules were modelled as point atoms. The first, at N(1), was modelled as disordered over two sets of positions with a major occupancy of 50.9(6)%. That at N(2) was modelled at half-weight. There is two-fold disorder modelled for the phenyl ring at C(45) > C(50) which forms part of the benzilic acid group at O(10) and (O11). The major occupancy is 52.4(8)%. One OnPr group at O(19) was modelled with two-fold disorder in one CH₂ group and the major occupancy is 70.6(11)%.

Figure S15. Two, almost perpendicular, views of 8.8MeCN.

Figure S16. Difference electron density map for $8 \cdot 8(C_2H_3N)$.

For $8 \cdot 8(C_2H_3N)$: $V_8(O)_4K_{0,30}(On-Pr)_8[Ph_2C(OH)(CO_2)]_{12} \cdot 8(C_2H_3N)$. The overall core structure is basically the same as $7 \cdot 7$ MeCN. In all cases, the OH H atoms needed to be included in a constrained manner with either rotational freedom or aligned to make the most reliable H-bond. The one unique MeCN that was refined as point atoms, was modelled as disordered over two sets of positions with major occupancy 51.1(8) %. Where MeCN H atoms were not modelled due to the disorder, they are included in the formula. Atom C(86) at On-Pr group containing O(19) was also modelled as two-fold disordered with major occupancy 72.1(13) %. Platon squeeze recovered 135 electrons in each of two voids interpreted as 6 MeCNs per void and per V_8

complex.

Compound	1	2.2MeCN	3.8MeCN	4.3 75MeCN	5.6 38MeCN
	-		C. H. Na O.V.:	C. H. Na. V.O.:	C H Na VO
Formula	$C_{36}H_{44}N_2O_{10}V_2$	$C_{40}H_{52}N_{2}O_{10}V_{2}{\cdot}2MeCN$	8MaCN	$C_{184}\Pi_{172}\Pi_{0.74} \vee_8 O_{48}$	$C_{192}\Pi_{188}\Pi_{0.45}\Psi_{8}O_{48}$
Formula weight	766.61	004.82	4016.61	2720 77	2042 41
Formula weight	/00.01	904.82	4010.01	3/29.//	3943.41
Crystal system	Orthornombic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Pbca	Pī	$P2_1/n$	<i>P2</i> ₁ / <i>c</i>	P2 ₁ /n
Unit cell dimensions					
<i>a</i> (Å)	11.9119(9)	11.7706(6)	21.392(4)	21.5339(3)	21.4100(2)
<i>b</i> (Å)	15.6223(12)	12.4661(6)	19.182(3)	36.8417(6)	19.24118(15)
<i>c</i> (Å)	19.5264(15)	16.8513(9)	25.315(5)	25.4428(4)	25.4130(3)
α (°)	90	74.0119(8)	90	90	90
β (°)	90	83.5385(8)	110.694(2)	108.623(2)	111.1170(12)
γ (°)	90	72.0988(8)	90	90	90
$V(Å^3)$	3633.7(5)	2260.9(2)	9718(3)	19128.1(6)	9765.95(18)
Z	4	2	2	4	2
Temperature (K)	150(2)	150(2)	150(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.6904	1.54178	1.54178
Calculated density (g.cm ⁻³)	1.401	1.329	1.373	1.295	1.341
Absorption coefficient (mm ⁻¹)	0.57	0.47	0.42	3.79	3.74
Transmission factors					
(min./max.)	0.566, 0.889	0.745, 0.907	0.948, 0.980	0.540, 1.000	0.174, 1.000
Crystal size (mm ³)	$1.12\times0.24\times0.21$	$0.66 \times 0.36 \times 0.21$	$0.13 \times 0.12 \times 0.05$	0.44 imes 0.12 imes 0.04	$0.30 \times 0.30 \times 0.10$
$\theta(\max)$ (°)	30.6	30.5	25.0	68.2	67.1
Reflections measured	40423	26875	79020	175601	171151
Unique reflections	5538	13507	18641	34845	17412
R _{int}	0.040	0.019	0.113	0.087	0.075
Reflections with $F^2 > 2\sigma(F^2)$	4648	10955	10210	23854	14474
Number of parameters	234	559	1241	2578	1464
$R_1 [F^2 > 2\sigma(F^2)]$	0.041	0.039	0.107	0.106	0.072
wR_2 (all data)	0.109	0.109	0.353	0.324	0.219
GOOF, S	1.06	1.05	1.02	1.03	1.04
Largest difference peak and hole (e Å ⁻³)	0.57 and -0.34	0.71 and -0.49	1.13 and -1.02	1.85 and –1.04	1.14 and -0.51

$Table \ S1. \ Crystallographic \ data \ for \ 1-8.$

Compound	6·4MeCN	7·7MeCN	8.8MeCN
Formula	$C_{192}H_{188}Na_{0.77}O_{48}V_8\cdot$	$C_{192}H_{188}K_{0.2}O_{48}V_8\cdot$	$C_{192}H_{188}K_{0.3}O_{48}V_8\cdot$
Formula	4MeCN	7MeCN	8MeCN
Formula weight	3852.78	3966.13	4010.98
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_{1}/n$	$P2_{1}/n$	$P2_1/n$
Unit cell dimensions			
<i>a</i> (Å)	21.1654(11)	21.378(3)	21.3446(3)
<i>b</i> (Å)	19.0447(11)	19.274(3)	19.2640(2)
<i>c</i> (Å)	25.1144(15)	25.446(4)	25.4589(3)
α (°)	90	90	90
β (°)	110.027(12)	111.554(2)	111.1787(14)
γ (°)	90	90	90
$V(Å^3)$	9511.2(10)	9752(3)	9761.2
Z	2	2	2
Temperature (K)	100(2)	120(2)	100(2)
Wavelength (Å)	1.54178	0.6943	1.54178
Calculated density (g.cm ⁻³)	1.345	1.351	1.365
Absorption coefficient (mm ⁻¹)	3.83	0.42	3.80
Transmission factors (min./max.)	0.635, 1.000	0.930, 0.979	0.553, 0.971
Crystal size (mm ³)	$0.20\times0.08\times0.04$	$0.17 \times 0.15 \times 0.05$	$0.11 \times 0.07 \times 0.03$
<i>θ</i> (max) (°)	50.4	27.5	70.1
Reflections measured	94666	94774	94168
Unique reflections	9963	24018	18364
$R_{ m int}$	0.212	0.112 0.069	
Reflections with $F^2 > 2\sigma(F^2)$	7333	14591	13788
Number of parameters	1338	1267	1197
$R_1 [F^2 > 2\sigma(F^2)]$	0.150	0.079	0.069
wR_2 (all data)	0.429	0.253	0.212
GOOF, S	1.04	1.02	1.03
Largest difference peak and hole (e Å ⁻³)	1.13 and -0.97	1.22 and -0.99	0.79 and -0.52

Table S1 continued.

Comparison with crown ethers.

Figure S17. Crown ether diameters and alkali-metal ionic radii.

Structure	Central metal ion	V(1)…V(4) Å	V(2)…V(3) Å	O(23)…O(23A) Å	O(24)…O(24A) Å
(5)	Na⁺	3.375	3.389	6.056	6.097
(6)	Na⁺	3.401	3.408	5.999	6.031
(7)	K+	3.354	3.371	6.056	6.154
(8)	K+	3.3667	3.377	6.056	6.101

Table S2. Cavity dimensions for 5 - 8.

Figure S18. TGA for 8.8MeCN

Data were collected on a PerkinElmer TGA 400 using PyrisTM software and a rate of 10 °C per min over the 30 °C to 800 °C under N_2 . Sample weights were typically between 3 and 5 mg.

S19. Representative Figure SEM results: top $\{V_8(O)_4Na_{0.74}(OEt)_8[Ph_2C(OH)(CO_2)]_{12}\}\cdot 3.75 MeCN; (\textbf{4}\cdot 3.75 MeCN), calculated value for sample and the sample of the sample of$ dried in-vacuo (*i.e*. 3.75MeCN) minus = 0.48%; bottom $\{V_8(O)_4K_{0.30}(OnPr)_8[Ph_2C(OH)(CO_2)]_{12}\}$ ·8(MeCN) (8 ·8MeCN), calculated value for sample dried

in-vacuo (*i.e.* minus MeCN) = 0.32%. Data was recorded on a Zeiss EVO 60, using the sample in the form of a 12 mm diameter disc.

Figure S20. ¹H NMR spectrum of representative PCL (from entry 11, Table 1).

Figure S21. MALDI-ToF spectra of PCL using 1 at 130 °C under N₂ (entry 4, table 1). Present are chain polymers of the type H-PCL-OH, Na⁺ [M = 17 (OH) + 1(H) + n × 114.14 (CL) + 22.99 (Na⁺)] (e.g. peak 3122 = $(27 \times 114.14) + 23 + 18$), and a smaller series for cyclic PCL/Na⁺ [M = n × 114.14 (CL) + 22.99 (Na⁺)] (e.g. peak 3104 = $(27 \times 114.14) + 23$).

Figure S22. MALDI-ToF spectra of PCL using 1 as a melt under N₂ (entry 9, table 1). Present are chain polymers of the type H-PCL-OEt, Na⁺ [M = 45 (OEt) + 1(H) + n × 114.14 (CL) + 22.99 (Na⁺)] (e.g. peak 2466 = $(21 \times 114.14) + 23 + 46$), and a smaller series for cyclic PCL/Na⁺ [M = n × 114.14 (CL) + 22.99 (Na⁺)] (e.g. peak 2417 = $(21 \times 114.14) + 23$).

Figure S23. MALDI-ToF spectra of PCL using 2 at 130 °C under air (entry 15, table 1). Present are chain polymers of the type H-PCL-OH, Na⁺ [M = 17 (OH) + 1(H) + n × 114.14 (CL) + 22.99 (Na⁺)] (e.g. peak $3122 = (27 \times 114.14) + 23 + 18$).

Figure S24. MALDI-ToF spectra of PCL using 2 as a melt under air (entry 17, table 1). Present are chain polymers terminated by OH/ONa⁺ [M = 17 (OH) + 1(H) + n × 114.14 (CL) + 22.99 (Na⁺)] (e.g. peak 2780 = $(24 \times 114.14) + 23 + 18$), and a smaller series for cyclic PCL/Na⁺ [M = n × 114.14 (CL) + 22.99 (Na⁺)] (e.g. peak 2762 = $(24 \times 114.14) + 23$).

Figure S25. MALDI-ToF spectra of PCL using 8 at 130 °C under N₂ (entry 18, table 1). Present are chain polymers of the type H-PCL-OH, Na⁺ [M = 17 (OH) + 1(H) + n × 114.14 (CL) + 22.99 (Na⁺)] (e.g. peak 2780 = $(24 \times 114.14) + 23 + 18$) together with chain polymers of the type H-PCL-OnPr, Na⁺ [M = 59 (OnPr) + 1(H) + n × 114.14 (CL) + 22.99 (Na⁺)] (e.g. peak 2882 = $(24 \times 114.14) + 23 + 1 + 59$), and a smaller series for H-PCL-OMe, Na⁺ [M = n × 114.14 (CL) + 1(H) + 31 (OMe) + 22.99 (Na⁺)] (e.g. peak 2794 = $(24 \times 114.14) + 23 + 31 + 1$).

Figure S26. MALDI-ToF spectra of PCL using 8 as a melt under N₂ (entry 20, table 1). Present are chain polymers terminated by OH/O*n*Pr [M = 59 (OC₃H₇) + 1(H) + n × 114.14 (CL) + 22.99 (Na⁺)] (e.g. peak 2251 = $(19 \times 114.14) + 23 + 60$), and a smaller series for 2 OH [M = 17 (OH) + 1(H) + n × 114.14 (CL) + 22.99 (Na⁺)] (e.g. peak 2324 = $(20 \times 114.14) + 23 + 18$).

Figure S27. Kinetic run for 1.

Figure S28. Kinetic run for 2.

Figure S29. Kinetic run for 4.

Figure S30. Kinetic run for 8.

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