VIP **Vanadium(III) Compounds**

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Synthesis of Molecular Vanadium(III) Phosphonates[**]

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Dedicated to Professor Karl Wieghardt on the occasion of his 65th birthday

High-valent vanadium(IV/V) (organo)phosphates are common and are important in several areas.[1] Solid-state 3D phosphates have found use in catalysis,[2] while 2D inorganic–organic layered phosphonates can act as size-selective sorbents.[3] Molecular (0D) examples tend to have sphere- or bowl-like topologies, displaying remarkable host–guest chemistry[4] and even encapsulating anionic and cationic guests simultaneously, as in $[2\,NH_4^+,2Cl^-\subset V_{14}O_{22}(OH)_4(H_2O)_2(PhPO_3)_8]^{6-}$ reported by Müller et al.[5] Low-valent vanadium(III) and mixed-valence vanadium(III/IV) phosphonate phases are much rarer, and, with one exception, all of the known examples are extended lattice systems; see, for example, the work of Zubieta and co-workers and of Clearfield and co-workers.[1,6] Thus, the glaring omission from this class of materials is discrete molecular V^{III} and $V^{III/IV}$ phosphonates—to our knowledge the only known example is Salta and Zubieta's $(Ph_4P)(Bu_4N)[(V^{IV}O)_6V^{III}\{BuP(O)_2OPO_3\}_6]$.[7] After our work on other classes of V^{III} cages[8] and studies by us and others on using phosphonates to make Fe^{III} and $Mn^{II/III/IV}$ cages,[9,10] we show herein that such species can in fact be made readily, in contrast to predictions that the V^{III} ion will favor extended lattices in such materials due to its regular octahedral geometry.[1,6b]

The starting materials for this work are solid VCl_3 or the adduct $[VCl_3(thf)_3]$, which have been treated with a variety of phosphonates under ambient pressure and solvothermal conditions. When a slurry of VCl_3 in MeCN is treated with one equivalent of $Ph_3CPO_3H_2$ in MeCN with pyridine (py) and NEt_3 as base, $[V^{III}_4(\mu_4\text{-}O)(\mu\text{-}OH)_2(O_3PCPh_3)_4(py)_4]$ (**1**) is formed (Figure 1). The structure indicates formation of a distorted tetrahedron of V^{III} centers bound to a central μ_4-oxide ligand. Each face of the tetrahedron is capped by a 3.111 bridging phosphonate (Harris notation[11]). The cage shows a D_{2d} distortion from a perfect tetrahedron, with opposite edges of the tetrahedron having a μ-hydroxide group inserted into the V···V edge. The V sites are all six-coordinate, bound to the central μ_4-oxide ligand, a μ_2-OH group, three O atoms from phosphonates, and a terminal pyridine ligand.

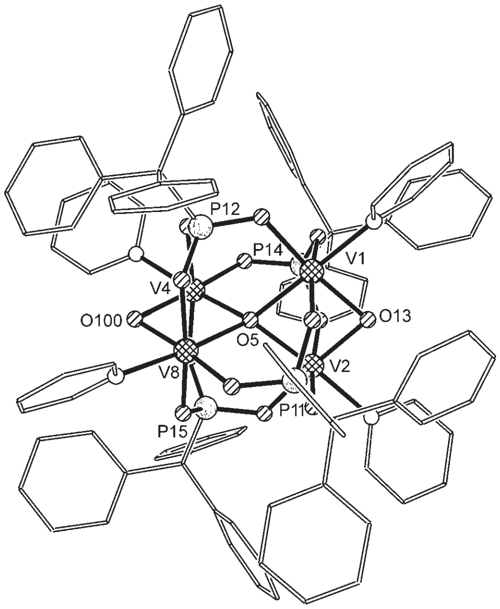

Figure 1. The structure of **1** in the crystal.

If the less sterically demanding *tert*-butylphosphonate is used in the same chemistry, $[V^{III}_5(\mu_3\text{-}OH)(O_3P\mathit{t}Bu)_6Cl_2(py)_6]$ (**2**) forms (Figure 2). In this structure, the V^{III} sites lie on the

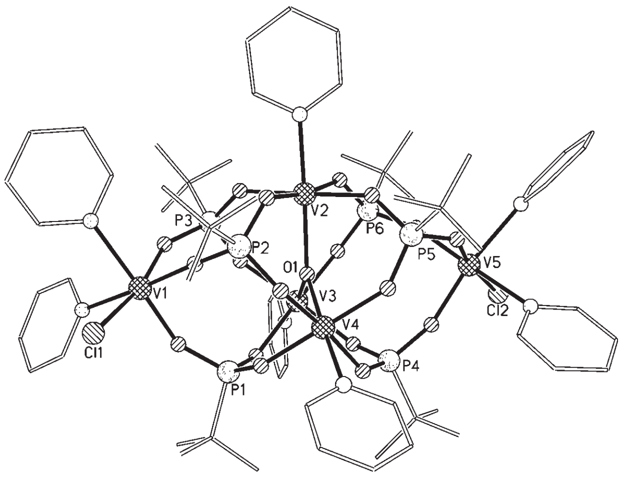

Figure 2. The structure of **2** in the crystal.

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vertices of a trigonal bipyramid. As in **1**, the phosphonates adopt the 3.111 mode and hence occupy the triangular faces of the polyhedron. Each equatorial V^{III} center (V2, V3, V4) is bound to four phosphonate O atoms, a μ_3-OH group, and a terminal pyridine ligand. Each apical V^{III} center is bound to one O atom from each of three phosphonates, two terminal pyridine ligands, and a terminal chloride ion. Charge balance is an issue with **2**; charges balance if the μ_3-O atom is from a hydroxide moiety, but not if it is an oxide ligand. This site is planar, but the V–O bond lengths are rather long (2.149–2.171 Å). Therefore, we have chosen the option which allows charge balance.

If pivalic acid is added to a slurry of VCl_3 prior to addition of *tert*-butylphosphonate, the hexanuclear cluster $[V^{III}_6(\mu_3\text{-}O)_2(O_2CtBu)_8(HO_2CtBu)_2(HO_3PtBu)_2(O_3PtBu)_2]$ (**3**) forms. This compound contains two oxo-centered vanadium(III) triangles linked by two 4.211 bridging phosphonates and two 2.110 bridging hydrogenphosphonates (Figure 3). The structure is directly analogous to a known hexanuclear Mn^{III} cage;[10d] however, the manganese analogue was made from reaction of an oxo-centered triangle with a phosphonate.

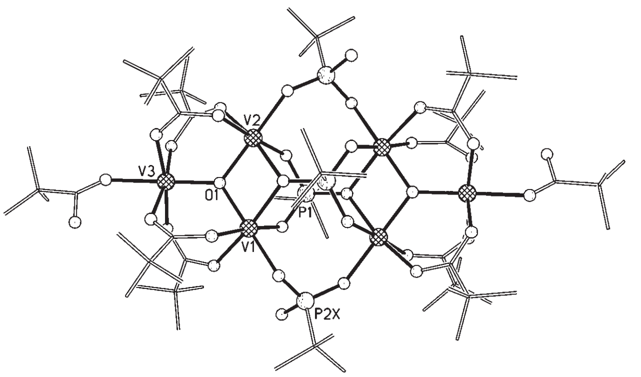

Figure 3. The structure of **3** in the crystal.

A much more unusual reaction occurs if **3** is heated solvothermally in MeCN. The compound reacts to give a nonanuclear V^{III} cage, $[V^{III}_9(\mu_3\text{-}O)_4(O_3PtBu)_3(O_2CtBu)_{13}]$ (**4**). Compound **4** has two analogues in Fe^{III} chemistry, both of which use pivalate as the carboxylate but with either camphylphosphonate[9d] or phenylphosphonate.[9b] In both cases, the nonanuclear iron(III) cages were made from oxo-centered triangles.

The structure of **4** is a tridiminished icosahedron of V^{III} sites, with phosphonates adopting the 5.221 bridging mode (Figure 4). If the V and P sites are taken together, they form a complete icosahedron. The metal sites can also be broken into two fragments, a $\{V_3O\}$ oxo-centered triangle and a $\{V_6O_3\}$ triangle of oxo-centered triangles. These two fragments are then linked through phosphonates.

The majority of carboxylates in **4** bridge the edges of the various metal triangles, adopting the 2.11 bridging mode. One carboxylate adopts the 3.21 mode, and this carboxylate breaks the noncrystallographic three-fold symmetry of the cage.

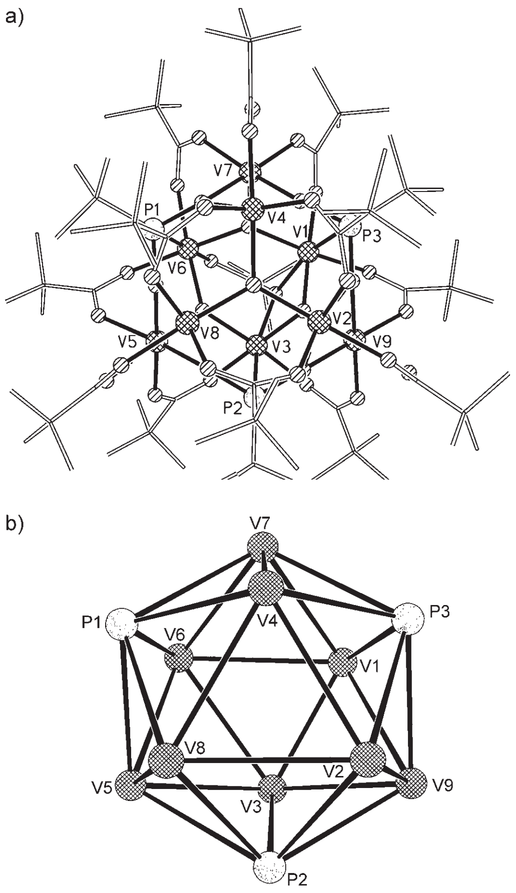

Figure 4. a) The structure of **4** in the crystal; b) the core icosahedron formed by vanadium and phosphorus.

Changing the solvent to alcohol leads to much larger cages. Reaction of $[VCl_3(thf)_3]$, $tBuPO_3H_2$, and benzoic acid with KOEt as base in EtOH under solvothermal conditions leads to $[V^{III}_{12}(V^{IV}O)(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_8(\mu_2\text{-}OEt)_4(EtOH)_4(PhCO_2)_4(O_3PtBu)_8]Cl_2$ (**5**). Compound **5** crystallizes on a crystallographic mirror plane (which passes through V5, V7, and V8) and is best described as a square of $\{V^{III}_3O\}$ triangles with a central vanadyl ion (V7) bound to the center of this cage (Figure 5). The square of triangles is formed such that eight V^{III} centers are in one plane (V1, V2, V3, V4, and their symmetry equivalents), and the remaining four V^{III} ions form a square above this octagon. The phosphonates adopt two bridging modes; four (those including P1 and symmetry equivalent, P3, and P4) bind in a 3.111 fashion on a face of each triangle. The other four (those including P2 and P5 and symmetry equivalents) link the triangles and adopt the 4.211 mode.

The vanadyl site is bridged by four μ-OH ligands to the four V^{III} centers within the square plane. Each of these V^{III} ions has a terminal EtOH ligand, all of which H-bond to one of the Cl^- counterions. The octagonal plane is reminiscent of $\{V_8\}$ rings reported with carboxylate ligands,[8a] in that the bridging on each edge of the octagon alternates. On four edges, the bridge is a 3.111 phosphonate, an ethoxide moiety, and the μ_3-OH ligand from a triangle. On the other four edges, the bridge is a 4.211 phosphonate, a μ-carboxylate, and a μ-OH group. The four hydroxide ligands lie towards the center of the cavity and H-bond to the second Cl^- ion (Cl···O

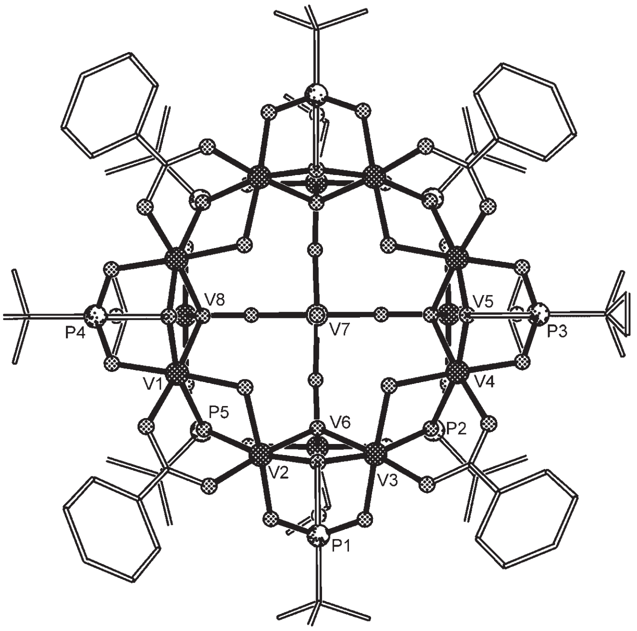

Figure 5. Structure of the cation of **5** in the crystal. See Figure S1 in the Supporting Information for the full structure including counterions and for polyhedral views.

ca. 3.1 Å). If deprotonated, these hydroxide groups, together with the oxide O atom from the central vanadyl ion, form a potentially pentadentate oxygen cavity. If a metal were to lie in this cavity, the M···O distance would be around 2.6 Å to the square of hydroxide ligands and 2.4 Å to the vanadyl oxygen atom.

Bond valence sum (BVS) calculations confirm that, with one exception, the vanadium centers in **1**–**5** are in the +3 oxidation state (valence sums 2.9–3.1, see the Supporting Information). The exception is the V7 site in **5**, which is in the +4 oxidation state (valence sum 4.2), which is easily recognized from the V=O bond length of 1.7 Å. BVS also supports assignment of all the μ_2- and μ_3-oxygen ligands in **5** as OH (see the Supporting Information). Preliminary magnetic susceptibility (χ) measurements on **3**–**5** are consistent with the assignment of oxidation states (Figure 6).

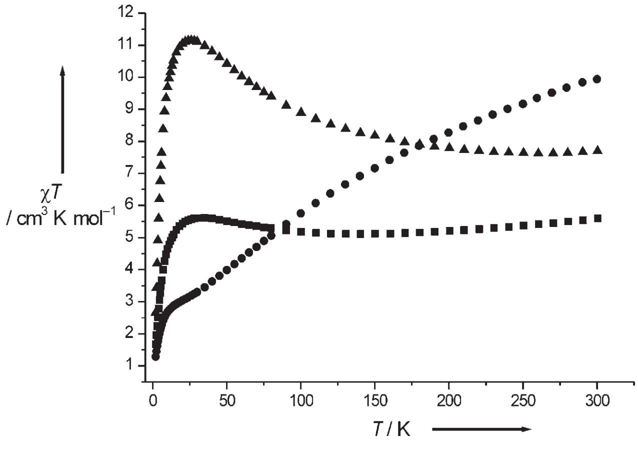

Figure 6. χT vs. T plots for complexes **3** (■), **4** (▲), and **5** (●).

The formation of **1**–**5** shows that molecular (0D) V^{III} (organo)phosphates can be prepared by simple routes. Indeed, the synthesis of these materials is more facile than our previous work on phosphonate cages of trivalent manganese[10] and iron[9a,b], in which we began with oxo-centered carboxylate triangles. **3**–**5** suggest that with V^{III}, we can form the triangles in situ, which is more convenient than preparing and isolating the air-sensitive $\{V_3O\}$ precursors.

It has been noted that the remarkable diversity of vanadium (organo)phosphate structures, and therefore function, is due to the unique structural variability of vanadium in its several accessible oxidation states and is further enhanced by the bridging tetrahedral (organo)phosphate groups.[1] It is our hope that by extending this class of materials to molecular V^{III} species we can extend the useful properties to include magnetism, for example as single-molecule magnets[12] exploiting the large magnetic anisotropy of the V^{III} ion. Preliminary studies are promising: variable-temperature data suggest high-spin ground or low-lying excited states for **3** and **4** and a low half-integer spin ground state for **5** (Figure 6). Detailed studies and analysis are underway.

Experimental Section

All reagents were used as received from Aldrich. $[VCl_3(thf)_3]$ was made by literature procedures. All manipulations were performed under anaerobic conditions. Elemental analyses for C,H,N,P,Cl were determined by standard combustion methods; those for V were determined separately by inductively-coupled plasma optical emission spectrometry (ICP-OES). For complex **4**, we could not get reasonable agreement for V content by this method, possibly owing to matrix problems.

1: A solution of $Ph_3CPO_3H_2$ (0.5 g, 1.54 mmol), Et_3N (0.31 g, 3.08 mmol), and pyridine (0.5 mL) in CH_3CN (10 mL) was added to a suspension of VCl_3 (0.24 g, 1.54 mmol) in CH_3CN (5 mL) at RT. The resultant green solution was stirred for 24 h and filtered. After three weeks, green crystals[13,14] of **1** were obtained (11 %).

2: A solution of tBuPO$_3$H$_2$ (0.34 g, 2.5 mmol), Et_3N (0.25 g, 2.5 mmol), and pyridine (0.5 mL) in CH_3CN (10 mL) was added to a suspension of VCl_3 (0.39 g, 2.5 mmol) in CH_3CN (5 mL) at RT. The resultant green solution was stirred for 24 h and filtered. After 12 weeks, green crystals of **2** were obtained (less than 5 %). Elemental analysis calcd (%) for $C_{65}H_{98}V_5N_{10}O_{19}Cl_2P_6$: C 42.54, H 5.38, N 7.63, P 10.12, V 13.88; found: C 41.21, H 5.15, N 6.83, P 10.19, V 13.52.

3: A solution of tBuCO$_2$H (1.02 g, 10 mmol) and Et_3N (1.3 mL, 10 mmol) in CH_3CN (20 mL) was added to a suspension of VCl_3 (0.78 g, 5 mmol) in CH_3CN (5 mL) at RT. The resultant slurry was heated to boiling for about 10 min, after which a solution of tBuPO$_3$H$_2$ (0.12 g, 0.83 mmol) and Et_3N (0.08 g, 0.83 mmol) in CH_3CN (5 mL) was added. The reaction mixture was stirred for 24 h and filtered. After two weeks, green crystals of **3** were obtained (28 %). Elemental analysis calcd (%) for $C_{70}H_{136}V_6N_2O_{34}P_6$: C 42.48, H 6.93, N 1.42; found: C 44.53, H 7.1, N 1.13.

4: Complex **3** (0.20 g, 0.10 mmol) in CH_3CN (9 mL) was heated at 150 °C in a sealed Teflon-lined autoclave to give green crystals of **4** following slow cooling (35 %). Elemental analysis calcd (%) for $C_{77}H_{144}V_9O_{39}P_3$: C 41.19, H 6.46, P 4.14, V 20.42; found: C 40.21, H 6.18, P 4.15, V 15.52.

5: $[VCl_3(thf)_3]$ (0.6 g, 1.6 mmol), tBuPO$_3$H$_2$ (0.138 g, 1 mmol), $PhCO_2H$ (0.061 g, 0.5 mmol), and KOEt (0.2 g, 2.5 mmol) in EtOH (14 mL) were heated at 150 °C in a sealed Teflon-lined autoclave for 12 h then cooled to give an insoluble solid under a green solution, which was filtered. Green crystals of **5** grew from the filtrate after two weeks (33 %). Elemental analysis calcd (%) for $C_{82}H_{168}V_{13}O_{57}P_8Cl_2$:

C 32.23, H 5.58, P 8.13, Cl 2.33, V 21.73; found: C 33.71, H 6.08, P 7.74, Cl 2.63, V 20.15.

Magnetic susceptibility (5 kG and 1.0 T applied fields) measurements were performed on polycrystalline samples on a Quantum Design MPMS SQUID magnetometer. Data are corrected for diamagnetic contributions according to the Pascal constants.

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[13] Crystal data for **1**·1.75 MeCN·0.25 H_2O: $C_{99.5}H_{85.75}N_{5.75}O_{15.25}P_4V_4$, $M_r = 1933.63$, $0.11 \times 0.11 \times 0.06$ mm^3, green plate, triclinic, space group $P\bar{1}$, $a = 18.652(4)$, $b = 20.154(2)$, $c = 26.782(5)$ Å, $\alpha = 72.45(3)$, $\beta = 85.23(3)$, $\gamma = 82.78(3)°$, $V = 9512(3)$ Å^3, $Z = 4$, $T = 150(2)$ K, λ(synchroton) = 0.69040 Å, $\rho_{calcd} = 1.35$ g cm^{-3}, 74340 reflections collected, 33461 unique ($R_{int} = 0.0604$), R(F) = 0.0647 and $wR2 = 0.1840$ using 26920 reflections with $I > 2\sigma(I)$. Crystal data for **2**·3 MeCN: $C_{65}H_{98}N_{10}O_{19}P_6V_5Cl_2$, $M_r = 1834.95$, $0.23 \times 0.15 \times 0.08$ mm^3, green block, monoclinic, space group Cc, $a = 26.149(5)$, $b = 13.331(3)$, $c = 49.308(10)$ Å, $\beta = 97.84(3)°$, $V = 17028(6)$ Å^3, $Z = 8$, $T = 150(2)$ K, $\rho_{calcd} = 1.432$ g cm^{-3}, λ(synchroton) = 0.69040 Å, 65309 reflections collected, 29674 unique ($R_{int} = 0.0615$), R(F) = 0.0444 and $wR2 = 0.1106$ using 27284 reflections with $I > 2\sigma(I)$. Crystal data for **3**·2 MeCN: $C_{70}H_{136}N_2O_{34}P_4V_6$, $M_r = 1979.33$, $0.35 \times 0.15 \times 0.03$ mm^3, green block, triclinic, space group $P\bar{1}$, $a = 11.968(2)$, $b = 15.409(3)$, $c = 15.761(3)$ Å, $\alpha = 69.32(3)$, $\beta = 69.96(3)$, $\gamma = 77.72(3)°$, $V = 17028(6)$ Å^3, $Z = 1$, $T = 100(2)$ K, $\rho_{calcd} = 1.294$ g cm^{-3}, λ(synchroton) = 0.17073 Å, 25127 reflections collected, 12935 unique ($R_{int} = 0.0349$), R(F) = 0.0493 and $wR2 = 0.1428$ using 9748 reflections with $I > 2\sigma(I)$. Crystal data for **4**: $C_{77}H_{144}O_{39}P_3V_9$, $M_r = 2245.29$, $0.23 \times 0.11 \times 0.04$ mm^3, green block, monoclinic, space group $P2_1/n$, $a = 26.4735(18)$, $b = 15.6272(11)$, $c = 28.8611(19)$ Å, $\beta = 110.381(10)°$, $V = 11192.6(13)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\rho_{calcd} = 1.332$ g cm^{-3}, λ(synchroton) = 0.78480 Å, 76831 reflections collected, 19704 unique ($R_{int} = 0.1078$), R(F) = 0.0685 and $wR2 = 0.1693$ using 12032 reflections with $I > 2\sigma(I)$. Crystal data for **5**·3 EtOH: $C_{82}H_{168}V_{13}O_{57}P_8Cl_2$, $M_r = 3047.04$, $0.1 \times 0.1 \times 0.1$ mm^3, green block, monoclinic, space group $P2_1/m$, $a = 13.559(5)$, $b = 28.725(13)$, $c = 18.759(3)$ Å, $\beta = 110.238(9)°$, $V = 6855(4)$ Å^3, $Z = 2$, $T = 150(2)$ K, $\rho_{calcd} = 1.476$ g cm^{-3}, λ(synchroton) = 0.69070 Å, 6503 reflections collected, 6503 unique ($R_{int} = 0.000$), R(F) = 0.1256, $wR2 = 0.3107$ using 4435 reflections with $I > 2\sigma(I)$. CCDC 639860–CCDC 639864 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/data_request/cif.

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