Stepwise assembly of a polyoxovanadate from mononuclear units in an organic solvent: carboxylate-stabilised fragments in the conversion of $[VOCl_4]^{2-}$ to $[V_{15}O_{36}]^{5-}$

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The $[VOCl_4]^{2-}$/AgOAc reaction system in MeCN gives $[V_5O_9Cl(OAc)_4]^{2-}$, $[V_9O_{19}(OAc)_5]^{3-}$ and $[V_{15}O_{36}]^{5-}$ for reagent ratios of 1:2, 1:3 and 1:4, respectively: the V_5 and V_9 cores are fragments of the V_{15} core, suggesting the V_5 and V_9 units are carboxylate-stabilised intermediates in the assembly of the V_{15} polyoxovanadate.

Polyoxometalates represent a venerable and greatly explored area of early transition metal chemistry.[1–4] They are of interest from a variety of viewpoints, including structural aesthetics,[1–4] routes to new materials,[5–7] catalysis[8] and medical applications,[9] to name but a few. These molecular species often possess cage-like structures and in many cases encapsulate a small neutral or charged group.[3,4,10] One such example (amongst many) is the encapsulation of Cl^-, Br^- or CO_3^{2-} 'guests' within the approximately spherical $[V_{15}O_{36}]^{5-}$ polyoxovanadate 'host' cage.[11]

The steps by which a polyoxometallate such as $[V_{15}O_{36}]^{5-}$ assembles and the precise importance of the encapsulated guest to the identity and stability of the host are important to know. Bowl-like polyoxovanadates that can be considered structural fragments of (and putative intermediates to) cage-like structures are rarely encountered but one such example is approximately hemispherical $[V_{12}O_{32}(MeCN)]^{4-}$ containing an MeCN molecule in the concave cavity.[12] In the somewhat related field of fullerene chemistry, the preparation of structural fragments of the fullerene cage, so-called buckybowls, is a very topical area.[13] In this report, we describe the development of methodology that allows possible intermediates in the assembly of the $[V_{15}O_{36}]^{5-}$ cage to be stabilized by carboxylate ligands and identified. This approach has also provided access to the empty $[V_{15}O_{36}]^{5-}$ cage, a host without a guest.

The reaction of $[NEt_4]_2[VOCl_4]$ **1** with 2 equiv. of NaOAc in MeCN under nitrogen, followed by brief exposure to air gives a deep green solution from which can be obtained $[NEt_4]_2[V_5O_9Cl(OAc)_4]\cdot MeCN$ **2** ($4V^{IV},V^{V}$) in 20–25% yield: this procedure is analogous to that previously reported for $[NEt_4]_2[V_5O_9Cl(O_2CPh)_4]$.[14] A related reaction using AgOAc in place of NaOAc and omitting the aerial oxidation step also gives **2** in comparable yield. Increase of the $[VOCl_4]^{2-}$:AgOAc reaction ratio to 1:3 gave instead a blue solution which, after *ca.* 50% volume reduction *in vacuo* and filtration, slowly produced dark blue–black crystals of $[NEt_4]_3[V_9O_{19}(OAc)_5]\cdot 2MeCN$ **3** ($5V^{IV}$, $4V^{V}$) in 20–30% yield.† Further increase of the reaction ratio to 1:4 gave a purple solution which, after *ca.* 50% volume reduction and filtration, produced dark purple–black crystals of $[NEt_4]_5[V_{15}O_{36}]\cdot 1.28MeCN$ **4** ($8V^{IV}$, $7V^{V}$) in 45–50% yield.† The anion of **2** (Fig. 1)‡ has the same $[V_5O_9Cl]^{2+}$ core reported previously[14] for $[V_5O_9Cl(O_2CPh)_4]^{2-}$, with a V_5 square-pyramid (V^{V} at the apex) and O^{2-} and Cl^- ions triply and quadruply bridging the vertical and basal faces, respectively. The novel $[V_9O_{19}]$ core of **3** (Fig. 2) may be considered an extension of the core of **2**, giving an approximately hemispherical bowl that contains an *anti,anti*-bridging AcO^- group. This is reminiscent of $[V_{12}O_{32}(MeCN)]^{4-}$ where a MeCN molecule is held inside a bowl.[12] The other AcO^- groups are like those in **2**, *i.e.* bridging V···V edges of the $[V_xO_y]$ unit and blocking further aggregation. The $[V_{15}O_{36}]^{5-}$ anion of **4** (Fig. 3) is a known polyoxovanadate, but in this case it is empty, previous examples containing an anionic guest ion inside the cage.[11]

Given the similar synthetic procedures to **2**–**4**, it is reasonable to suggest that the $[V_5O_9]$ and $[V_9O_{19}]$ cores of **2** and **3** may be

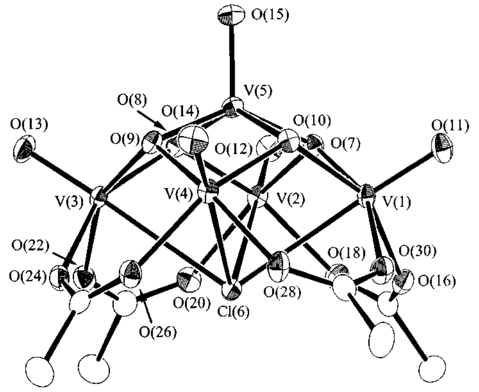

Fig. 1 ORTEP representation with 50% probability ellipsoids of the $[V_5O_9Cl(OAc)_4]^{2-}$ anion of **2**.

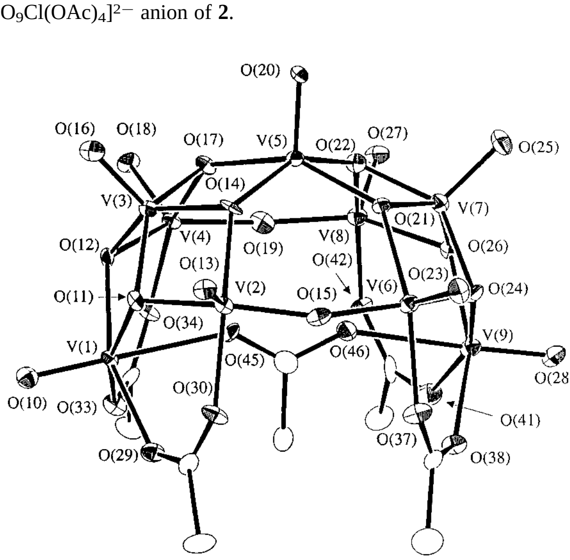

Fig. 2 ORTEP representation with 50% probability ellipsoids of the $[V_9O_{19}(OAc)_5]^{3-}$ anion of **3**.

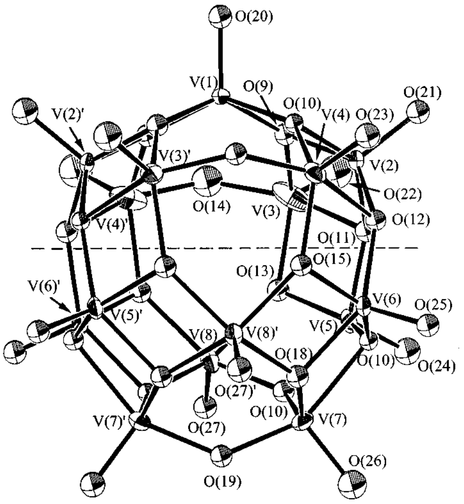

Fig. 3 ORTEP representation with 50% probability ellipsoids of the $[V_{15}O_{36}]^{5-}$ anion of **4**. The $[V_7O_{17}]$ portion of the structure above the dashed line is the same as in the anion of **3** (Fig. 2).

considered carboxylate-stabilised intermediates in the assembly of the $[V_{15}O_{36}]^{5-}$ ion of **4** in MeCN, and that the minimal sequence in its formation is that in eqn. (1). This is supported by

$$[VO]^{2+} \rightarrow [V_5O_9]^{3+} \rightarrow [V_9O_{19}]^{2+} \rightarrow [V_{15}O_{36}]^{5-} \qquad (1)$$

the structural relationship between the $[V_9O_{19}]$ core and $[V_{15}O_{36}]^{5-}$ (Fig. 3). A common $[V_7O_{17}]$ unit is seen: in **3**, the O atoms at left and right of this [O(11)/O(12) and O(24)/O(26) of Fig. 2] bind to only two V atoms [V(1) and V(9)], whereas in **4** they bind to four V atoms [V(5), V(5)′, V(6), V(6)′ of Fig. 3] allowing the $[V_{15}O_{36}]$ shell to form. Interestingly, the complete $[V_9O_{19}]$ core of **3** is a fragment of the $[V_{18}O_{42}]$ cage-like polyoxovanadate with T_d symmetry.[4] Note that the acetate O atoms of **2** and **3** occupy sites that would otherwise be occupied by O^{2-} ions giving higher nuclearity products. The AgOAc reagent that causes formation of **2–4** from **1** clearly has multiple functions: (i) as a source of AcO^- groups both to stabilise the fragments in **2** and **3** *and* to act as Brønsted bases to facilitate formation of O^{2-} ions from H_2O molecules [O : V ratios are 1 : 1 (**1**), 1.8 : 1 (**2**), 2.1 : 1 (**3**) and 2.4 : 1 (**4**)]; (ii) as a Cl^- abstracting reagent; and (iii) as an oxidizing agent [average V oxidation states are 4+ (**1**), 4.2+ (**2**), 4.44+ (**3**) and 4.47+ (**4**)]. It is thus reasonable that the AgOAc : **1** ratio is so important. Indeed, treatment of redissolved **3** in MeCN with additional AgOAc gives a colour change from blue to purple and subsequent crystallisation of **4**.

The solid-state effective magnetic moment (μ_{eff}) of **3** gradually decreases from 3.62 μ_B at 300 K to 3.15 μ_B at 2.00 K. For **4**, μ_{eff} gradually decreases from 2.86 μ_B at 300 K to 2.67 μ_B at 30.0 K, and then increases slightly to 2.83 μ_B at 3.00 K. Fitting of magnetization data collected in the 0.05–5 T and 2.00–4.00 K ranges gave $S = 3/2$, $g = 1.70$ and $D = 0.00$ cm^{-1} for **3** and $S = 3/2$, $g = 1.62$ and $D = 0.00$ cm^{-1} for **4**. The magnetic properties of $[V_5O_9Cl(O_2CR)_4]^{2-}$ species such as **2** have been previously described.[14] More detailed analysis of the exchange interactions in **3** and **4** will be provided elsewhere.[15]

The formation of **2–4** from **1** suggests that stepwise control of the assembly of polyoxometallates may indeed be feasible by suitable choice of solvent and reagents (and their ratios) allowing access to a variety of bowl-like species. Further experimentation along these lines is in progress.

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Notes and references

† Further volume reduction or addition of *e.g.* Et_2O gives significantly greater yields of **3** and **4** but the coloured products are contaminated with white solids. The described procedures avoid this but at the expense of large yields. Dried solids are hygroscopic and analysed satisfactorily (C, H, N).

‡ *Crystal data*: **2**·MeCN: $C_{26}H_{55}ClN_3O_{17}V_5$, $M_r = 971.89$, monoclinic, space group $C2/c$, $a = 16.111(2)$, $b = 14.900(2)$, $c = 33.674(5)$ Å, $\beta = 91.39(1)°$, $U = 8081$ Å^3, $Z = 8$, $T = 101$ K, $R(R_w) = 0.0361$ (0.0411) using 6432 reflections with $F > 3\sigma(F)$.

3·2MeCN: $C_{38}H_{81}N_5O_{29}V_9$, $M_r = 1530.55$, triclinic, space group $P\bar{1}$, $a = 13.303(1)$, $b = 23.031(1)$, $c = 10.804(1)$ Å, $\alpha = 90.81(1)$, $\beta = 111.91(1)$, $\gamma = 94.15(1)°$, $U = 3060$ Å^3, $Z = 2$, $T = 109$ K, $R(R_w) = 0.0773$ (0.0563) using 5037 reflections with $F > 2.33\sigma(F)$. One cation lies on a non-crystallographic mirror plane, disordering its four CH_2 carbon atoms about two well resolved positions.

4·1.28MeCN: $C_{42.56}H_{103.84}N_{6.28}O_{36}V_{15}$, $M_r = 2043.92$, monoclinic, space group $C2/c$, $a = 22.105(3)$, $b = 13.784(2)$, $c = 26.604(4)$ Å, $\beta = 107.56(1)°$, $U = 7728$ Å^3, $Z = 4$, $T = 101$ K, $R(R_w) = 0.1111$ (0.1125) using 4190 reflections with $I > 2.33\sigma(I)$; the MeCN molecules and three of the cations were badly disordered.

CCDC 182/1440. See http://www.rsc.org/suppdata/cc/1999/2249/ for crystallographic files in .cif format.

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