A high-nuclearity, beyond "fully reduced" polyoxo(alkoxo)vanadium(III/IV) cage

Ian S. Tidmarsh,[a] Rebecca H. Laye,[a] Paul R. Brearley,[a] Maheswaran Shanmugam,[a] E. Carolina Sañudo,[a] Lorenzo Sorace,[b] Andrea Caneschi[b] and Eric J. L. McInnes*[a]

Received (in Cambridge, UK) 10th April 2006, Accepted 4th May 2006
First published as an Advance Article on the web 18th May 2006
DOI: 10.1039/b605106e

The solvothermal synthesis, crystal structure and preliminary magnetic studies are reported of the first high nuclearity V^{III}-based polyoxo(alkoxo)vanadium cage, a $V^{III}_{16}V^{IV}_2$ complex.

Given the large amount of literature on high-valent vanadium(IV/V) clusters—the polyoxo(alkoxo)vanadates—and their important redox, catalytic and magnetic properties,[1–3] it is surprising that there is a dearth of literature on their low valent V^{III} or mixed $V^{III/IV}$ analogues. Indeed a "fully reduced" polyoxo(alkoxo)vanadate is usually taken to mean one containing d^1 ions—the magnetic behaviour of these have attracted much interest,[3,4] for example Müller's V^{IV}_{15} clusters.[3] Lower valent species could have considerable promise as magnetic materials[5,6] exploiting the large magnetic anisotropy of the d^2 V^{III} ion,[7] or as powerful reducing agents[8] exploiting the high concentration of low-valent ions. Although the existence of solid state V^{III} and mixed-valence $V^{III/IV}$ oxides, oxy- and oxyfluoro-phosphate materials[9] suggests that molecular clusters should be isolable, there are only three reports of V^{III} (and none of $V^{III/IV}$) clusters of any type containing more than four metal ions[10–12] and these contain little or no inorganic oxide. Presumably it is the easily oxidisable nature of the V^{III} ion that is responsible for the lack of examples. Therefore, the first challenge in their study is how to prepare them. Here we report the synthesis of an octadeca-metallic $V^{III}_{16}V^{IV}_2$ species by a simple solvothermolysis reaction of monomeric $[V(acac)_3]$ and $[VO(acac)_2]$ precursors ($acac^-$ = acetylacetonate). The molecular product contains sixteen V^{III} ions, capped by two vanadyls, has a 1 : 1 ratio of V : O(H) and can be considered the first example of a highly reduced, $V^{III/IV}$ polyoxovanadium cage.

Reaction of $[V(acac)_3]$ with benzoic acid (4 : 1) in EtOH at 150 °C for 12 h under an inert atmosphere, followed by slow cooling, gives brown crystals in low yield direct from the reaction solution. These are shown by X-ray crystallography to be $[V_{18}(O)_{12}(OH)_2(H_2O)_4(EtO)_{22}(O_2CPh)_6(acac)_2]$ (**1**).† **1** is centrosymmetric and the structure can be described as two opened-tetrahedral V^{III}_4 units linked to two square-based pyramidal $V^{III}_4V^{IV}$ fragments (Fig. 1). The V_4 units [V6,V7,V8A,V9 and symmetry equivalents (s.e.)] consist of four edge-sharing $\{VO_6\}$ octahedra, centred on a μ_4-oxide (O5A and s.e.) and bound by five μ_2-ethoxides. The V–O5–V angles range from 98.1(2)–102.2(2)° with the exception of 148.9(3)° which opens the V7–O5A–V8A edge. The two V_4 units are fused along the O4···O6 and s.e. edges (also bridged by μ_2-benzoates) to form an octametallic core (Fig. 1c,d). The pentametallic units (V1–5 and s.e.) consist of five edge-sharing $\{VO_6\}$ octahedra defining a square-based pyramid with V2 at the apex, bound by a μ_5-oxide (O1), six μ_2-ethoxides and two μ_3-oxides (O2, O3). V2 has a terminal oxide (O15), and one of the basal ions (V1) has a chelating $acac^-$. Surprisingly, these are the only diketonates in the structure despite the high concentration in the reaction. V3 and V4 have terminal waters.

One basal vanadium ion (V5) in each of the pentametallic units in **1** links to the octametallic core through four vertex-sharing interactions (O2,O3,O4,O6A; Fig. 1d). O4 and O6A are μ_3 and also bind both tetrametallic units to V5; O2 and O3 are μ_3, near-planar and each link one tetrametallic unit (*via* V6 or V9, respectively) to an edge of a pentametallic unit (V3···V5 or V4···V5, respectively). Bond valence sum (BVS) analyses of the oxide environments indicate that O4, which is significantly non-planar, is in fact hydroxide while O1, O2, O3 and O6 are oxide. Although O4 and O6 perform the same bridging role, the V–O4 distances are significantly larger than V–O6 consistent with protonation. **1** has two vanadium(IV) ions as vanadyl (V2 and V2A), easily identifiable by their terminal V=O distances of *ca.* 1.62 Å, which are at the apices of the pentametallic units. BVS of all other vanadium ions are consistent with the +3 oxidation state.

Hence, **1** is a $V^{III}_{16}V^{IV}_2$ cluster—by far the largest low-valent valent vanadium cluster reported to date (see below). The two V^{IV} ions in **1** must be due to serendipitous oxidation of $[V(acac)_3]$ in the original preparation. Much higher yields of **1** are obtained from a more rational solvothermal reaction including a V^{IV} source: reaction of $[V(acac)_3]$, $[VO(acac)_2]$ and $PhCO_2H$ (8 : 1 : 3) in EtOH to give **1** in *ca.* 30% yield.‡ **1** cannot be isolated from analogous reactions under reflux or at room temperature.

In contrast to the previously known high nuclearity V^{III} clusters $[V_8(OH)_4(OEt)_8(O_2CR)_{12}]$, $[V_{10}(OMe)_{20}(O_2CMe)_{10}]$ and $[V_7MF_8(O_2CR)_{16}]^+$ (M = divalent metal ion),[10–12] which contain little or no inorganic (hydr)oxide, the 1 : 1 V : O(H) ratio in the $\{V^{III}_{16}V^{IV}_2O_{12}(OH)_2(OH_2)_4\}$ inorganic core of **1** means that it can be classed as a highly reduced polyoxo(alkoxo)vanadate (although "vanadate" strictly implies an anionic species). Indeed, although the overall structure is unique, the topologies of its building blocks have precedent in high-valent polyoxometallates. The tetrametallic fragments are type **IVb** structural units in Zubieta's classification.[2] These fuse to form the octametallic core, related to the well known edge-sharing bioctahedral decametallate $\{M_{10}O_{28}\}$ structure[2] with removal of two metal ions from the shared edge, as has been observed previously for Mo in $[Mg_2Mo_8O_{22}(OMe)_6(MeOH)_4]^{2-}$.[13] V5 and V5A have "slipped" away from the V_8 core, freeing two

---

[a] *School of Chemistry, The University of Manchester, Manchester, UK M13 9PL. E-mail: eric.mcinnes@manchester.ac.uk; Fax: +44-(0)161-275-4616; Tel: +44-161-275-4469*
[b] *Department of Chemistry, Poloscientifico, Florence, Italy*

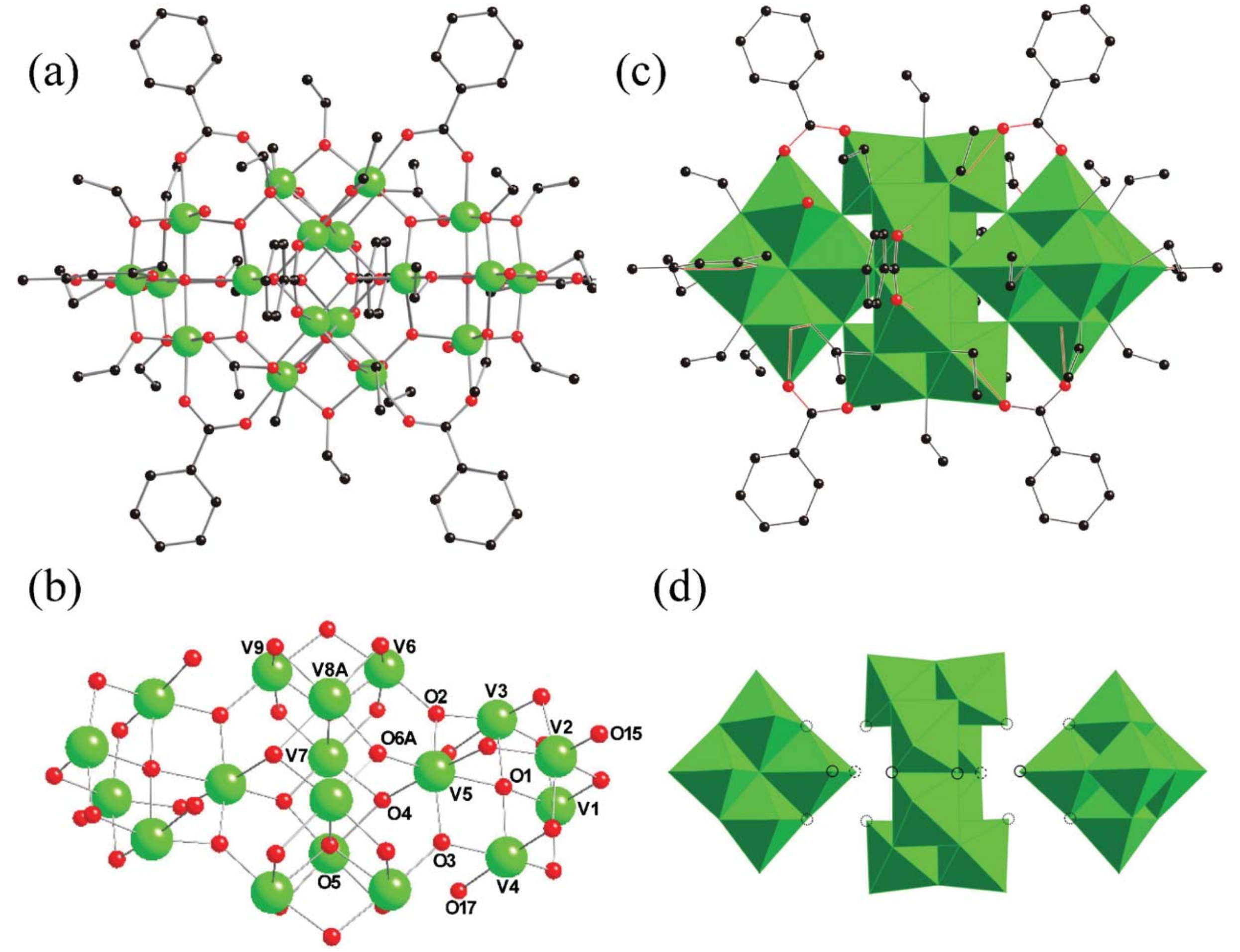

Fig. 1 (a) Molecular structure, and (b) vanadium oxide core, of $[V_{18}(O)_{12}(OH)_2(H_2O)_4(EtO)_{22}(O_2CPh)_6(acac)_2]$ (**1**). Selected bond length ranges (Å): V2–O15 1.619(9), V–(μ_4-)O5 1.923(5)–2.015(5), V–(μ_3-)O4(H) 2.092(5)–2.305(5), V–(μ_3-)O6 1.919(5)–1.947(5), V–(μ_5-)O1 2.077(6)–2.191(6), V3,4–O(H_2) 2.288(9) and 2.291(9). *cis* V–O1–V angles range from 88.9(2)–97.0(2)°. Green (V), red (O), black (C), H omitted for clarity. Atoms labeled "A" indicate atoms at $(1 - x, 1 - y, 1 - z)$; (c) $\{VO_6\}$ polyhedral representation; (d) separated polyhedral representation of the core, showing the two pentametallic $V^{III}{}_4V^{IV}$ units and the octametallic core formed from two $V^{III}{}_4$ units. The circles show common oxygen vertices between the fragments.

coordination sites to bridge further to form the pentametallic fragments which are Zubieta's type **V** structural units (Fig. 1d).[2]

Preliminary studies show the magnetic properties of **1** to be dominated by antiferromagnetic interactions. The room temperature χT value of 10.7 emu K mol^{-1} is well below that expected for 16 V^{III} and 2 V^{IV} uncoupled ions and is already decreasing rapidly with decrease in temperature, decreasing to *ca.* 1.8 emu K mol^{-1} at 2 K. These features imply very strong antiferromagnetic coupling, although we are unable to model this behaviour at present given the low symmetry and consequent large number of possible exchange interactions.

In summary, Zubieta has shown previously that substitution of oxo for alkoxide ligands can stabilise "fully reduced" d^1 polyoxovanadates, including by hydrothermal synthetic methods.[2] Here we have shown that d^2, vanadium(III)-based polyoxo(alkoxo)vanadium cages can be prepared through a simple solvothermal route using simple precursors in alcohols. This promises a new class of highly reduced species for study. Further studies on the magnetic and redox behaviour of **1** are in progress.

This work was supported by the EPSRC, The Leverhulme Trust, the EC (NMP3-CT-2005-515767 "Magmanet", HPMT-CT-2000-00179 "Molmag" and MRTN-CT-2003-504880 "QuEMolNa"), and Italian PRIN and FIRB projects.

Notes and references

† Crystal structure data for **1**: $C_{96}H_{164}O_{56}V_{18}$, Mr = 3131.91, crystal size 0.39 × 0.23 × 0.03 mm, triclinic, space group $P\bar{1}$, a = 14.0361(13), b = 16.0288(13), c = 16.2151(12) Å, α = 74.367(7), β = 87.552(7), γ = 65.633(9)°, V = 3190.4(5) $Å^3$, T = 100(2) K, Z = 1, ρ_{calcd} = 1.630 g cm^{-3}, $\mu(\lambda$ = 0.71073 Å) = 1.33279 mm^{-1}, 15920 reflections collected, 7765 independent (R_{int} = 0.0785), $R(F)$ = 0.0902 and $wR2$ = 0.2386 for $I > 2\sigma(I)$ [$R(F)$ = 0.1238, $wR2$ = 0.2793 for all data]. CCDC 299653. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605106e

‡ $[V(acac)_3]$ (0.72 mmol), $[VO(acac)_2]$ (0.09 mmol), $PhCO_2H$ (0.27 mmol) and EtOH (9 mL) were heated at 150 °C in a sealed Teflon-lined container for 12 h, followed by slow cooling to give crystals of **1** (*ca.* 30%). Elemental analysis calcd (%) for $C_{96}H_{164}O_{56}V_{18}$: C 36.82, H 5.28, V 29.28; found: C37.38, H 5.22, V 29.03%. Selected IR data (KBr pellet): cm^{-1} 2923.56 (w), 1596.17 (s), 1557.08 (s), 1415.09 (s), 1100.78 (s), 1058.37 (s), 969.96 (w), 898.37 (w), 717.05 (s), 597.26 (s). All manipulations were conducted under an inert atmosphere. **1** degrades rapidly on exposure to air. Freshly prepared **1** is soluble in dry CH_2Cl_2, but after storage for several days it loses crystallinity to yield an insoluble brown material. All analyses, including magnetic studies, were conducted on freshly prepared samples and were repeated on more than one batch. Samples were analysed before and after measurement to ensure integrity.

1 For example see: M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34; A. Müller, J. Meyer, H. Bogge, A. Stammler and A. Botar, *Chem.–Eur. J.*, 1998, **4**, 1388; J. Livage, *Coord. Chem. Rev.*, 1998, **178–180**, 999; J. Do, R. P. Bontchev and A. J. Jacobsen, *Inorg. Chem.*, 2000, **39**, 3230; C. Daniel and H. Hartl, *J. Am. Chem. Soc.*, 2005, **127**, 13987.

2 Q. Chen and J. Zubieta, *Coord. Chem. Rev.*, 1992, **114**, 107; M. I. Khan and J. Zubieta, *Prog. Inorg. Chem.*, 1995, 43.

3 A. Müller, F. Peters, M. T. Pope and D. Gatteschi, *Chem. Rev.*, 1998, **98**, 239; D. Gatteschi, L. Pardi, A.-L. Barra, A. Muller and J. Doring, *Nature*, 1991, **354**, 463.

4 K. Hegetschweiler, B. Morgenstern, J. Zubieta, P. J. Hagrman, N. Lima, R. Sessoli and F. Totti, *Angew. Chem., Int. Ed.*, 2004, **43**, 3436.

5 H. Weihe and H. U. Güdel, *J. Am. Chem. Soc.*, 1998, **120**, 2870; P. Knopp, K. Wieghardt, B. Nuber, J. Weiss and W. S. Sheldrick, *Inorg. Chem.*, 1990, **29**, 363.

6 S. L. Castro, Z. Sun, C. M. Grant, J. C. Bollinger, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1998, **120**, 2365.

7 P. L. W. Treggena-Piggott, H. Weihe, J. Bendix, A.-L. Barra and H. U. Güdel, *Inorg. Chem.*, 1999, **38**, 5928.

8 M. Sadakane and E. Steckhan, *Chem. Rev.*, 1998, **98**, 219.

9 G. Bonavia, R. C. Haushalter and J. Zubieta, *J. Solid State Chem.*, 1996, **126**, 292; R. C. Haushalter, Z. Wang, M. E. Thompson and J. Zubieta, *Inorg. Chem.*, 1993, **32**, 3700.

10 R. H. Laye, M. Murrie, S. Ochsenbein, A. R. Bell, S. Teat, J. Raftery, H. U. Güdel and E. J. L. McInnes, *Chem.–Eur. J.*, 2003, **9**, 6215.

11 R. H. Laye, F. K. Larsen, J. Overgaard, C. A. Muryn, E. J. L. McInnes, E. Rentschler, V. Sanchez, S. J. Teat, H. U. Güdel, O. Waldmann, G. A. Timco and R. E. P. Winpenny, *Chem. Commun.*, 2005, 1125.

12 H. Kumagai and S. Kitagawa, *Chem. Lett.*, 1996, 471.

13 M. Yu. Antipin, L. P. Didenko, L. M. Kachapina, A. E. Shilov, A. K. Shilova and Y. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 1989, 1467.