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A Highly Reduced Vanadium(III/IV) Polyoxovanadate Comprising an Octavanadyl Square-Prism Surrounding a Dimetallic Vanadium(III) Fragment

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"Fully reduced" polyoxo(alkoxo)vanadates—usually taken to mean those exclusively containing d^1 metal ions, often stabilized by organic capping ligands—are rather rare[1,2] compared to their d^0 analogues but have attracted significant interest due to their important redox[3] and magnetic[4] properties. However, more highly reduced examples containing d^2 ions remain elusive, beyond simple tri- or tetrametallic species, despite their obvious potential in these areas. We have been developing the use of 1,2,3-triazoles as rigid bridging ligands to generate paramagnetic cage complexes with useful magnetic properties, with successes including iron(III) clusters with huge electronic spin ground states,[5] and we have now started to explore their chemistry with the vanadium(III) ion in an effort to isolate low-valent vanadium cages. Here we report our preliminary results in this area, with the unexpected formation of a highly reduced vanadium(III/IV) polyoxovanadate. This complex is remarkable because of the following: (i) it is based on a square-prismatic, boxlike cluster of oxovanadium(IV). The square-based topology, unique for a polyoxometalate, is generated via the 1,3-bridging mode of the triazole, analogous to the role of 4,4′-bipyridine in the self-assembly chemistry of molecular squares;[6] (ii) the oxovanadium(IV) "box" contains a covalently bound vanadium(III) dimer to give an overall very highly reduced polyoxovanadate. Preliminary magnetic studies are reported.

Reaction of $\mathrm{VCl_3}$ (0.25 g) with 5,6-dimethylbenzotriazole ($\mathrm{Me_2btaH}$; 0.46 g) and NaOMe (0.17 g) in MeOH (30 mL) at room temperature under an inert atmosphere for 18 h followed by reduction of the volume and layering with anhydrous, degassed diethyl ether gives orange-brown crystals of **1** (10%).[7] Single-crystal X-ray diffraction[7] reveals **1** to be the mixed-valence $\mathrm{V^{III/IV}}$ species $[(\mathrm{V^{IV}O})_8\mathrm{V^{III}_2(Me_2bta)_8(OH)_4(OMe)_{10}}]$ (Figure 1). The molecule lies on a 4/*mmm* site in the tetragonal *I*4/*mmm* space group, giving just two vanadium ions in the asymmetric unit.[8] One of these (V1) is $\mathrm{V^{IV}}$ as vanadyl, easily identified by the short terminal V═O distance 1.596 Å, and the remaining metal ion (V2) is $\mathrm{V^{III}}$ (see below). The polyhedron defined by the vanadyl ions is a perfect square-prismatic "box" with dimensions of 6.030(2) Å × 6.030(2) Å [V1⋯V1D and symmetry equivalents (s.e.)] × 2.954(2) Å (V1⋯V1A and s.e.), and with the terminal oxides oriented outward from the cluster.

The edges of the square faces of the $(\mathrm{VO})_8$ box are formed by 1,3-coordinated $\mathrm{Me_2bta^-}$ bridges. Four of these are μ_2-bridging, and four are μ_3 being further coordinated to a central vanadium ion (V2 or s.e.) via their middle, 2-nitrogen. The short edges of the box (V1−V1A and s.e.) are bridged by two μ_2-OMe (O2) and a μ_3-hydroxide (O3) which also binds to V2. O3 is trans to the terminal oxide resulting in a relatively long V1−O3 distance. O3 is distinctly nonplanar (V1−O3−V1A 81.58°, V1−O3−V2 128.1°; O3 is 0.54 Å out of the V1, V1A, V2 plane), and bond valence sum (BVS) analysis[9] supports formulation as hydroxide rather than oxide.[10]

The $(\mathrm{VO})_8$ box is bound to two internal V ions (V2, V2B) that form a $\mathrm{V_2(\mu_2\text{-}OMe)_2}$ dimer with a V2...V2B distance of 3.000(3) Å. V2 also binds to the two μ_3-$\mathrm{Me_2bta^-}$ on the edges of the box and to the hydroxides O3 and s.e. The coordination at V2 is pseudo-octahedral *cis*-$\mathrm{O_4N_2}$, and the metric parameters are consistent with

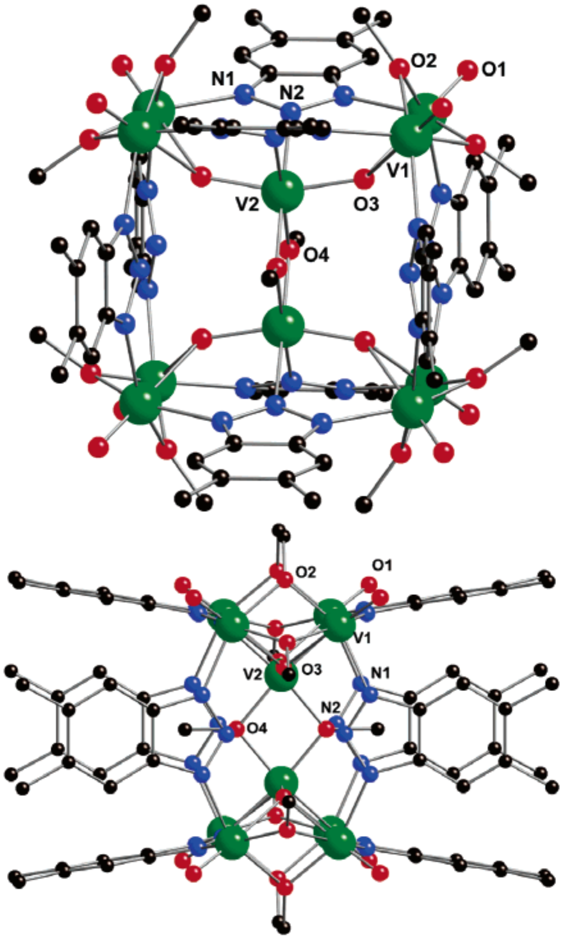

Figure 1. Molecular structure of $[(\mathrm{VO})_8\mathrm{V_2(Me_2bta)_8(OH)_4(OMe)_{10}}]$ (**1**) viewed (a) near-normal to the square face, (b) near side-on to the square face. Bond lengths at $\mathrm{V^{IV}}$ (Å): V═O 1.596(3), V−μ_2O(Me) 1.984(3), V−μ_3O 2.261(3), V−N(μ_2-$\mathrm{Me_2bta}$) 2.108(3). Bond lengths at $\mathrm{V^{III}}$ (Å): V−μ_3O 1.830(3), V−μ_2O(Me) 1.949(4), V−N(μ_3-$\mathrm{Me_2bta}$) 2.219(4). Selected interbond angles (deg): V1−O2−V1A 96.24(16), V1−O3−V1A 81.58(12), V1−O3−V2 128.10(3), V2−O3−V2E 70.84(17), V2−O4−V2F 100.6(2). V, green; O, red; N, blue; C, black; H omitted for clarity. See Supporting Information Figure 1 for full labeling of symmetry equivalent positions.

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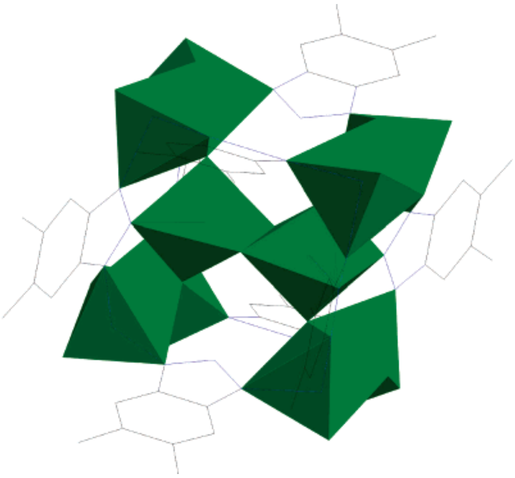

Figure 2. Polyhedral representation of **1**: green octahedra are *cis*-$\{O_4N_2\}$ coordination spheres at each V.

formulation as V^{III}, confirmed by BVS analysis, as is also required by charge balance. This is also consistent with the magnetic data (see below).

A polyhedral representation shows that the pairs of ions on the short edges of the $(VO)_8$ square-prism form face-sharing bioctahedra, each of which vertex shares via a single oxide with the central edge-sharing bioctahedron of V^{III} (Figure 2).

The formation of a vanadyl cluster was unexpected and is presumably due to serendipitous oxidation of the V^{III} starting material. Although we have subsequently found that **1** can also be prepared from more rational reactions of $\{VO\}^{2+}$, V^{III}, and Hbta reagents [solvothermal reaction of $(VO)SO_4$ (0.7 mmol), VCl_3 (0.7 mmol), and Hbta (2.6 mmol) in MeOH (6 mL) at 100 °C], the yields are not significantly improved from the original preparation (ca. 12%). It is the formation of the cage by partial oxidation of V^{III} precursors that has allowed us to isolate a very highly reduced, $V^{IV}_8V^{III}_2$, polyoxovanadate; we are not aware of any examples with more than four metal ions in the literature to date. Indeed low oxidation state vanadium clusters of any description are rare,[11,12] although solid-state V^{III} and $V^{III/IV}$ phosphonates are known.[13] The oxidized ions form a cage round the reduced ions, and this may reflect the mechanism of formation, cluster growth being terminated by oxidation of vanadium and formation of terminal oxides.

The square faces of **1** result from four 1,3-bridging Me_2bta^- linking four metal ions via cis coordination sites, reminiscent of Stang and Fujita's M^{II}_4 molecular squares[6] exploiting rigid linear bridges such as 4,4′-bipyridine and metal ions with two available 90° *cis*-coordination sites in stoichiometric reactions. Che et al.[14] have argued that rigid *angular* bridges [e.g., the anion of benzimidazole, analogous to 1,3-coordinated bta^-] favor formation of triangles in such reactions. Our results show that this is an oversimplification, given the 130° angles between N−V vectors in the 1,3-coordinated triazole and N−V−N angles of 93° in **1**.

1 undergoes a quasi-reversible reduction at −0.93 V vs Fc/Fc^+ in 0.5 M $(^nBu_4N)BF_4/CH_2Cl_2$ solution, which we tentatively assign to $V^{III/II}$ by comparison with the similar potential observed for a bis-alkoxide bridged V^{III} dimer[15] and the fact that reduction of vanadyl to V^{III} is unlikely. No oxidative processes are observed. The magnetic properties of **1** are dominated by antiferromagnetic interactions: the room-temperature value of χT (χ = molar magnetic susceptibility) is 3.3 cm^3 Kmol^{-1}, below the value expected for eight V^{IV} and two V^{III} uncoupled ions, already rapidly decreasing with decreasing temperature and tending toward zero indicating a diamagnetic ground state (Figure S2). We have fitted $\chi(T)$ based on a three unique J-value model, considering only metal ions connected by single-atom bridges: between V^{IV} ions on the short edges of the box (J_1), between V^{IV} and V^{III} ions (J_2), and between the two V^{III} ions (J_3). This gives $J_1 = 246$ cm^{-1}, $J_2 = 39$ cm^{-1}, and $J_3 = 45$ cm^{-1} (all antiferromagnetic) with $g = 1.99$ (Figure S2). The strong J_1 is consistent with the face-sharing (i.e., three single-atom bridges) V^{IV} ions, while J_3 is within the range found for bis-alkoxide bridged V^{III} dimers.[16]

We are now attempting to isolate larger and more reduced (higher V^{III}/V^{IV} ratio) analogues of **1** by controlling the oxidation of the V^{III} precursors.

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Supporting Information Available: Full atom labeling (including disorder), χ and χT vs T and fits, thermal ellipsoid plot, cif file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Microanalysis of **1**: calcd for $C_{74}H_{98}N_{24}O_{22}V_{10}$: C, 40.67; H, 4.52; N, 15.38. Found: C, 40.58; H, 4.86; N, 14.47. X-ray details of **1**: $C_{74}H_{98}N_{24}O_{22}V_{10}$, 2185.16, tetragonal, *I*4/*mmm*, orange crystal, $a = b = 17.4950(18)$ Å, $c = 18.5306(19)$ Å, $T = 150$ K, $Z = 2$, $R = 0.0783$, GOF = 1.132.

(8) The molecule is disordered over two perpendicular orientations. This has no effect on the V^{IV} positions, but the two V^{III} ions are disordered over the two sites with 60:40 occupancy. These four partial occupancy sites were also observed when the crystal structure was solved in *P*1 so, although **1** has only two-fold symmetry, the structure was solved in a tetragonal space group as this was considered the more favorable for the packing of the metal ions. A similar disorder of a dimer over three perpendicular positions, being positioned on a special site in a high crystal symmetry, has been observed; see: Cotton, F. A.; Daniels, L. M.; Shang, M.; Yao, Z. *Inorg. Chim. Acta* **1994**, *215*, 103.

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(10) Figure 1a shows that there are large holes between O3 and the uncoordinated nitrogens where the protons could be accommodated. Thus, an alternative formulation of **1** is as $[(VO)_8V_2(Me_2bta)_4(Me_2btaH)_4(O)_4(OMe)_{10}]$ where the four μ_2-Me_2bta are protonated and O3 is oxide.

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