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Polyoxometalates

Nanoscale Growth of Molecular Oxides: Assembly of a {V_6} Double Cubane Between Two Lacunary {P_2W_{15}} Polyoxometalates**

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Polyoxometalates (POMs) are metal–oxygen clusters commonly consisting of W, Mo, and V.[1] They have a wide variety of applications in such areas as catalysis[2] and medicine[3] and also have wide ranging sizes and properties.[4] Addenda metal atoms in these clusters can be substituted with other transition metals, for instance the substitution of transition metals into polyoxometalates is a well-established area of the field.[5] Such transition-metal-substituted polyoxometalate (TMSP) clusters are of great interest since they can be used as secondary building blocks to give extended structures, such as dimeric sandwiches,[5a] trimers,[6] or even tetramers.[7] Furthermore, the design and assembly of TMSP clusters provides a platform for the systematic development of POM clusters with fundamentally new physical properties (e.g. magnetic),[8,9] or modulating and enhancing the redox properties and applications of the POM, for example in electron storage/redox processes.[10] However, most TMSPs are not amenable for processing into new materials and it is important to develop routes to producing TMSPs with tuneable redox properties that are compatible with organic solvents, or can be incorporated into organic-hybrids.

Herein we present a new organic-soluble vanadium-based Wells–Dawson sandwich compound, $(TBA)_{10}[P_4V_6W_{30}O_{120}]\cdot 4\,CH_3CN$ (**1**, TBA = $(n\text{-}C_4H_9)_4N$, Figure 1),[11] which contains a double cubane vanadium core with interesting electronic properties. This compound is unusual as it has six vanadium atoms embedded between the two lacunary Dawson clusters, where the majority of sandwich compounds have four hetero metal atoms.[5,12] It is also unique in that it is formed from pre-substituted lacunary clusters, with no additional transition metal added to the reaction, as generally the transition metal is added to the lacunary POM to provide a linked structure.

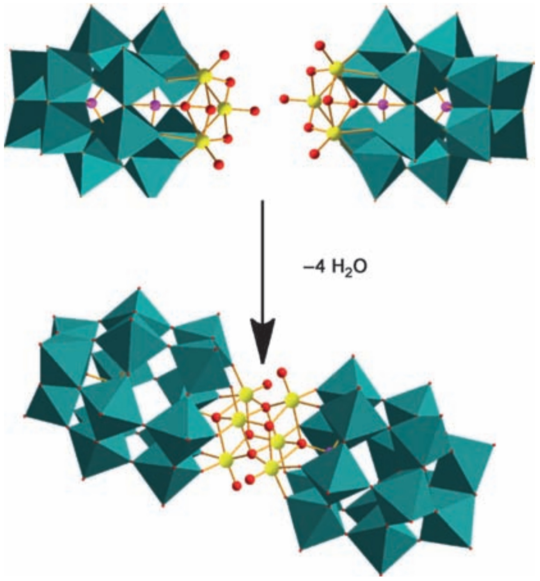

Figure 1. $(TBA)_{10}[P_4V_6W_{30}O_{120}]$ (**1**; bottom) with double cubane core. Green octahedra: WO_6, pink spheres: PO_4^{3-}, yellow spheres: V, red spheres: O. TBA counterions are omitted for clarity.

This method allows more control over the final structure, as the substituted metal ions are already in place. Despite intensive work carried out in the area of TMSPs, the assembly of new TMSPs in organic solvents using soluble precursors,[13,14] as well as those incorporating vanadium as the heterometal,[15] are rare. Also, double cubanes have rarely been seen in POMs before, with the only examples being Ni-substituted Keggin clusters[16,17] or a single-molecule magnet based on Mn-substituted Keggin clusters.[9] Finally, to probe the electronic properties of **1**, we present for the first time the technique of coupled spectro-electrochemistry/mass-spectrometry measurements to control the redox state of the cluster, and probe the stability of the cluster in solution.

The Wells–Dawson anion $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14\,H_2O$[18] is used to synthesize an organic-soluble TBA-trivanadium-capped Dawson cluster, $(TBA)_5H_4[P_2W_{15}V_3O_{62}]$, {$P_2W_{15}V_3$}.[19] This cluster is commonly used to create organically functionalized hybrid compounds. It is also possible to substitute one or two vanadium atoms into the Wells–Dawson framework. These compounds may be useful for such purposes as catalysis.[20]

Compound **1** is formed in good yield from the {$P_2W_{15}V_3$} precursor under simple reflux conditions. The product is easily obtained by precipitation from ether and is then crystallized by diffusion of ether into acetonitrile to give small

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yellow crystals in ca. 95 % yield, which were characterized by X-ray diffraction. This synthesis provides a structured approach to creating a larger architecture by reliably dimerizing the starting material with no side products, other than a little unreacted starting material, observed. The only change to the cluster is the conversion of four terminal oxygen atoms from the $\{P_2W_{15}V_3\}$ cluster to bridging oxo groups with the net loss of four water molecules as the cluster dimer forms. This reaction requires the loss of four protons per $\{P_2W_{15}V_3\}$ unit which are presumably located on the terminal oxo groups of the vanadium sites (i.e. as two hydroxo groups and one aqua group).[19] This indicates that the building blocks used are favorably organized to produce the dimer, but no other large architectures. The absence of other reactants and stability of the starting compound when refluxing in acetonitrile, as seen when attaching functional groups to the vanadium cap,[21] provides further evidence for the assembly of the cluster with no breakdown of the starting materials.

Compound **1** can be described structurally as having two α-isomers of $\{P_2W_{15}V_3\}$ linked together, with one $\{P_2W_{15}V_3\}$ rotated by 180°, giving the appearance of the two being slightly offset from each other. The slightly offset vanadium core consists of four of the six vanadium atoms having a terminal oxo bond and five bonds to bridging oxygen atoms. The other two contain six bonds to bridging oxygen atoms. The vanadium atoms can also be seen to form a vanadium face-sharing double cubane, as shown in Figure 2. The bond lengths in this cubane core are between 1.92 and 2.40 Å. The O-V-O bond angles for the corners are between 70.1(3) and 79.5(4)°, and the O-V-O bond angle connecting the two cubanes is 153.3(5)°.

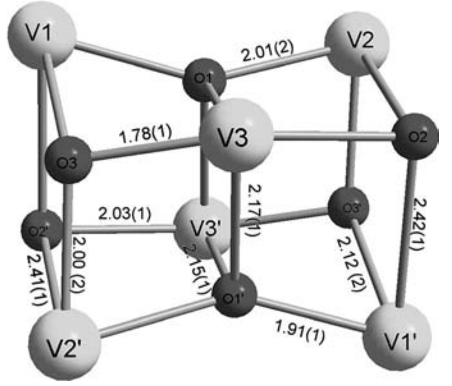

Figure 2. The double cubane vanadium core unit found in **1**. The double cubane core of the sandwich structure is shown with O-V-O bond lengths included. The majority of the bond angles are between 70.1° and 79.5°, with the exception of the vanadium atoms linking the cubanes, O3-V3-O2 and O2′-V3′-O3′, which are 153.3(5)° and the bond lengths are between 1.92 and 2.40 Å.

The double cubane consists of alternating V and O atoms, and is slightly compressed in the center, forming two connected, irregular cubes. From BVS (bond valence sum) calculations, redox measurement and elemental analysis, we can assign the oxidation state of the vanadium atoms as +5. Importantly, we can follow the reaction process by mass spectrometry. This is achieved by comparing the reaction mixture and a sample that was precipitated from acetonitrile with diethyl ether, and analyzed using ESI-MS over five consecutive days. The dimerization process is shown as the mass almost doubles and the charge also doubles giving two envelopes for both the starting and finishing cluster at almost the same *m*/*z* envelopes, showing the progressive increase in charge by the appearance of more highly charged peaks (Figure 3). This suggests the sandwich compound begins to form in the first day of the experiment and continues to grow in concentration until approximately the fifth day. The starting material peaks range in charge from 3− to 2− between *m*/*z* 1450 and 2500, whereas those of the product are between 6− and 3− over the range 1450 to 3500, indicating the presence of two $\{P_2W_{15}V_3\}$ clusters, rather than one. The peaks for the product either overlay peaks from starting material, meaning that a peak can contain envelopes of 3− and 6− or 4− and 2−, or create new peaks which consist entirely of product.

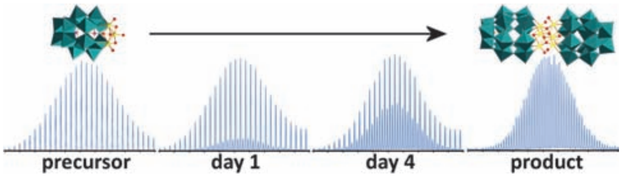

Figure 3. Example of a peak envelope from the reaction mixture as a function of time. The product, compound **1**, can be observed from day 1 and the ratio of product to starting material increases up to day 5 where the pure product can be isolated. The initial peak envelope (3−) corresponds to $(P_2W_{15}V_3O_{62})(TBA)(CH_3CN)_5H_5$ and the product peak (6−) to $(P_4W_{30}V^{V}_4V^{IV}_2O_{120})TBA_4H_2$; that is, the charge doubles for the mass so number of lines per mass unit increases. The scale is the same for each envelope (*m*/*z* 1467–1477).

The redox behavior of compound **1** was studied in acetonitrile solution (see Supporting Information, Figure S4) and this showed that the reduction of the six vanadium centers occurs simultaneously, giving a broad wave, with the corresponding E_c peak potentials located at −0.360 V. On reversal of the scan two vanadium-centered oxidation waves are observed at +0.110 V and +0.545 V. It is possible to assign these two waves to oxidation processes involving the V^{IV} centers of reduced **1**, as confirmed by potential-controlled coulometry. This indicated that, when the reduction is carried out at −0.7 V, just beyond the broad reduction peak, the process consumes 6.0 ± 0.5 electrons per molecule while the solution colour changed from yellow-orange to dark green. Although there are further features below −1 V that could be related to the reduction of some tungsten centers, it is rather difficult to be sure, presumably since the overall cluster complex is rather unstable after being reduced by six electrons and starts to decompose.

We also found that the compound is highly photoactive in both solution and in the solid state. For instance, if a degassed acetonitrile solution of **1** is illuminated for 24 h using a 150 W Xe lamp, the yellow solution of the fully oxidized compound becomes dark green. This is indicative of the formation of

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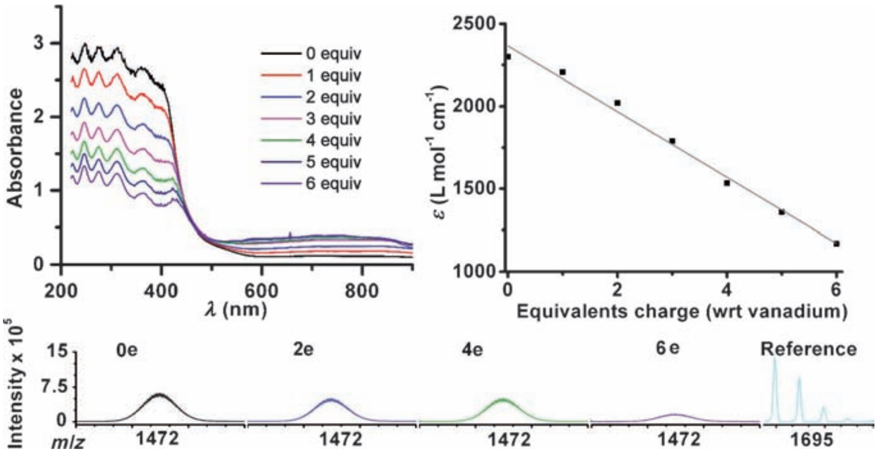

Figure 4. Correlation between the mass spectrum and UV/vis spectrum of **1** during electrochemical reduction. The molar extinction coefficients are calculated at 423 nm and a reference peak is used in the mass spectrum to compare the product peaks. The reference peak is assigned as $[(TBA)_4(PF_6)_5]^-$, which is subjected to the same experimental conditions as **1**.

reduced vanadium (see Supporting Information for the cyclovoltammetry (CV) and UV measurements). This data, particularly the CV, indicates that irradiation of compound **1** in acetonitrile solution causes partial decomposition and this is confirmed by mass spectrometry measurements (see Figure S2 and Table S2). This instability is probably due to the electrostatic repulsions within the double cubane core, forcing it to "break" into smaller fragments. Preliminary EPR measurements of the reduced species were carried out at various temperatures between 100 and 200 K, with a peak characteristic of vanadium(IV) appearing, with hyperfine coupling, at 100 K. However, at higher temperatures the peak cannot be seen, suggesting that electrons may be delocalized across all vanadium atoms in the cubane at these temperatures.

A further very interesting aspect is the photochemical behavior of the crystals of **1**. Under these conditions a single-crystal-to-single-crystal transformation occurs, whereby compound **1** becomes dark green to give compound **1′**. X-ray studies show that the gross structure of compound **1′** is the same as for **1**, but a BVS analysis indicates the $\{V_6\}$ cubane is approximately three to four electrons reduced and some of the oxygen atoms are now protonated (the source of the electrons appears to be the residual water present in the sample of **1**). This is confirmed electrochemically by the coulometric reoxidation of a powdered sample of **1′**, which indicated that the compound was indeed three to four electrons reduced (see Supporting Information).

To explore the electrochemical reduction of the compound further, and to explore the stability of compound **1** as it is reduced, we investigated the reduction process using a combination of spectroelectrochemistry coupled with ESI mass spectrometry (Figure 4).This is the first time these techniques have been combined. These studies revealed a trend in the mass spectrometry data showing a reduction in intensity of the peak envelope at 1472 (this is assigned as $(P_4W_{30}V^{V}_4V^{IV}_2O_{120})(TBA)_4H_2)$, which is found in the mass spectrum of compound **1** (Supporting Information) and can be compared against the internal standard, $[(TBA)_4(PF_6)_5]^-$. This comparison allows us to see that the concentration of the parent compound, **1**, decreases with increasing reduction, consistent with the molar extinction coefficients from the trend in the UV/vis spectra. The loss of product peak intensity in the mass spectrum data is also seen in material reduced chemically, using ascorbic acid. This shows peaks corresponding to both compound **1** and the precursor to **1**, $\{P_2W_{15}V_3\}$, indicating that compound **1** is broken down upon reduction of all the vanadium atoms, but can withstand reduction of some of the vanadium centers.

In conclusion, an organically soluble polyoxometalate sandwich structure, of formula $(TBA)_{10}[P_4V_6W_{30}O_{120}]\cdot 4CH_3CN$ with six linking metal atoms was synthesized from organically soluble transition-metal-substituted building blocks in good yield. The compound was shown to undergo facile reduction of the double cubane core by electrochemical, chemical, and photochemical processes up to three electrons. Future work will focus on investigating the electronic properties in organic solvents as well as attempting to engineer analogous double cubane clusters with Keggin rather than Dawson-based polyoxometalates. We will also expand the use of spectro-electrochemistry probed by ESI-MS, and in this case, explore the in situ fragmentation energies of the species as a function of redox state, as well as more fully explore the possible photoreactivity of the compound towards the oxidation of water.

Experimental Section

$(TBA)_5[H_4P_2W_{15}V_3O_{62}]$ was synthesized according to literature procedures.[19,20] $(TBA)_5[H_4P_2W_{15}V_3O_{62}]$ (1 g, 0.2 mmol) was dissolved in acetonitrile (30 mL) and refluxed for 5 days in the dark. The resulting mixture was filtered and added dropwise into an excess of diethyl ether (300 mL) with vigorous stirring. The resulting yellow powder was dried in a desiccator overnight. The dry powder was then dissolved in a minimum amount of acetonitrile and set up for diffusion with diethyl ether. After one week, yellow crystals were collected. Yield: 94.6 % based on $(TBA)_5[H_4P_2W_{15}V_3O_{62}]$. Elemental analysis calcd. (%) for $C_{160}H_{360}N_{10}O_{120}P_4V_6W_{30}$ (solvent lost): C 18.68, H 3.53, N 1.36, W 52.8, V 2.9; found: C 18.39, H 3.45, N 1.32, W 52.7, V 3.3. ^{1}H NMR (CD_3CN) showed peaks for TBA at $\delta = 3.20$, 1.69, 1.47, and 1.04 ppm.

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[11] Crystallographic data and structure refinements for formula $(\mathrm{TBA})_{10}[\mathrm{P_4V_6W_{30}O_{120}}]\cdot 4\,\mathrm{CH_3CN}$, $M_r = 10\,453.82$; block crystal: $0.18\times0.14\times0.04\ \mathrm{mm}^3$; monoclinic, space group $P2_1/c$ $a = 22.9198(8)$, $b = 19.5989(4)$, $c = 33.2443(10)$ Å, $\beta = 107.887(3)°$, $V = 14\,211.6(7)$ Å^3, $Z = 2$, $\rho = 2.443\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Cu}_{\kappa\alpha}) = 24.202\ \mathrm{mm}^{-1}$, $F(000) = 9712$. 67 465 reflections measured, 16 997 unique ($R_{\mathrm{int}} = 0.1292$), 1084 refined parameters, $R1 = 0.0642$, $wR2 = 0.1552$. Crystal data were measured on a Oxford Diffraction Gemini Ultra A diffractometer using $\mathrm{Cu}_{\kappa\alpha}$ radiation ($\lambda = 1.54184$ Å) at 150(2) K. CCDC 839709 (**1**) and 839710 (**1′**) 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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