Bridging the gap between solution and solid state chemistry in polyoxometalate chemistry: Discovery of a family of $[V_1M_{17}]$-based cages encapsulating two \{V$^{V\text{O}_4}$\} moieties†‡

Haralampos N. Miras,$^a$ De-Liang Long,$^a$ Paul Kögerler$^b$ and Leroy Cronin$^{*a}$

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A family of polyoxometalates with the composition $[H_2V_3M_17O_{62}]^{6−}$ features a Dawson-like architecture containing two tetrahedral $\{V^{V\text{O}_4}\}$ templates rather than main group hetero-anions ($\{PO_4\}$ or $\{SO_4\}$ etc.) typically associated with classical heteropolyacids, situated within a mixed-metal $\{M^{M\text{V}_{17}V^{V\text{O}_4}}\}$ cage and these clusters were first discovered using mass spectrometry.

Introduction

Polyoxometalates (POMs) are metal–oxygen clusters$^1$ of W, Mo, V and represent a class of inorganic materials with an almost unmatched range of structure types and physical properties, with applications in areas as diverse as biology$^2$ and catalysis. The self-assembly of clusters based on Mo, W, or V oxo anions gives rise to an almost unrivalled range of polyoxometalate cluster anions. The versatile nature of these clusters originates from the ability to polymerize metal-based polyhedra to form a range of clusters from low to high nuclearities.$^3,4$ In particular, the ability for molybdenum and tungsten-based systems to form very large clusters has been demonstrated by a number of nano-sized cluster systems with over 100 tungsten$^5$ and molybdenum$^6,7$ atoms in a single cluster molecule. Therefore it is not surprising that polyoxometalates have been subjected to a vast number of studies due to their attractive electronic and molecular properties that give rise to a variety of applications e.g. in catalysis,$^8,9$ magnetism,$^{10,11}$ redox chemistry,$^{12,13}$ medicine,$^{14,15}$ and materials science.$^{16–19}$ Despite this great range of cluster types and properties, the ability to assemble large cluster systems from smaller known building blocks in a predetermined way is a great challenge, as such routes could be a direct way to systematically control the overall cluster architecture and properties. This is because the understanding and manipulation of the self assembly processes that underpin the formation of POM clusters has to be an attractive route to enable the design of clusters and multi-functional materials, which take advantage of the unique physical properties associated with this extraordinary class of molecules.$^{20}$ In particular the highly acidic properties of the highly stable Keggin-type heteropolyanions (HPAs)$^{21}$ such as $[W_{12}O_{40}(PO_4)]^{3−}$ or the atom transfer$^{22}$ of vanadium-substituted polyoxoanions such as $[H_2V_2Mo_{12}O_{54}(PO_4)]^{4−}$ render polyoxometalates as functional cluster systems.$^{23,24}$ Therefore, properties like acidity and redox activity are critically dependent on the nature and the relative positions of the metal cations in the framework as well as the type of heteroanion template incorporated within the cluster framework.$^{25}$ Furthermore, the acid strength of HPAs decreases in the order $W > Mo > V$ but the oxidizing ability in the order $V > Mo > W$. Moreover, additional electrons introduced in homometallic heteropolyanions with unequivocal $d^0$ metal atoms can be localized on preferential sites.$^{26}$ The development of high sensitivity methods for the direct and controllable synthesis and characterization leading to well-defined mixed cluster architectures$^{27,28}$ whereby both the inner templates and outer skeleton can be functionalised with hetero-metals is thus of vital importance. Certainly the development of high nuclearity POMs, often with electrophilic ions (transition metals and lanthanide ions) has been used to control growth,$^{29,28}$ often in the presence of many species. However, techniques for the isolation of a series of high nuclearity POMs which encapsulate hetero-transition metals or lanthanide ions are still lacking.

The true enormity of this challenge can be further clarified when one realises the main route to synthesize POM clusters (large or small) often employs ‘one-pot’ reactions.$^{3,5}$ Therefore, the manipulation of some of the many reaction parameters often represents a straightforward, but rather tedious, route to new, self-assembled POM architectures. To overcome such problems, the design of larger architectures using POM building blocks as synthons could provide a step change in the design and assembly of such systems. This is because the ability to assemble large cluster systems from smaller known building blocks could be a direct way to systematically control the overall cluster architecture and properties while retaining the geometries of the building blocks. Thus, such building blocks of well-defined shape and connectivity might form the basis for work towards the growth of nanoscopic clusters of predetermined structure and function.$^{30}$ However, the major problem with this approach lies in establishing routes to produce reactive building blocks present in solution in significant concentrations that can be reliably utilized in the formation of larger architectures, without re-organization or isomerisation to other fragments. Access to such building blocks has been the major limitation in stepwise growth of W- and Mo-based POM clusters. Such limitations may be circumvented by adopting an
approach that kinetically stabilizes the building block in solution, thereby effectively preventing its reorganization to other structure types.29–33

One possible route to this goal is to use bulky organic cations to isolate a new structure type by virtue of the cations used to ‘encapsulate’ the new building blocks, thereby limiting their reorganization to simpler structural types.29–33 By trapping clusters during the self-assembly process it may be possible to restrain the cluster from reorganizing into other well-known structure types, see Fig. 1. Also, in many cases, synthetic strategies to isolate a new structure type by virtue of the cations used during the cluster assembly process in the presence of hetero-anions would not be easily isolated without prior detailed knowledge of the clusters present in the reaction solutions.

In an extension to this approach we also recently isolated a family of sulfate-based Dawson-type mixed-valence polyoxomolybdate \( \text{MoO}_3\text{(SO}_3\text{)}_2 \text{)}^{2-} \), using the same type of synthetic approach. Thus, the use of bulky organic cations in the formation of Mo-based POMs appears to restrict aggregation to the more highly symmetrical cluster types, allowing a fundamentally more diverse set of clusters and cluster-based building blocks to be isolated, that display unprecedented structural or physical features.

Herein, we present our very recent efforts, expand our approach to the isolation of new cluster types using ‘encapsulating’ and directing organo-cations using high resolution cryospray and electrospray mass spectrometry. In particular we are interested in the development of mixed metal clusters and replacing the cluster templates. By combining our synthetic approach with solution based techniques to characterise the new clusters we aim to discover new cluster types with the aim of controlling the cluster architecture formed. Ultimately the aim is to be able to design new cluster architectures based on POM building blocks.

**Results and discussion**

Here we present four new structures which can be formulated as \( \text{V}_2\text{[M}_n\text{V}_1] \) which have the \( \alpha \)-Dawson cluster framework, see Fig. 2. The Dawson-type structural motif is well known\(^{38}\) for its ability to encapsulate hetero-anions and in our approach we aimed to replace the hetero-anion templates in the classical Dawson-like clusters e.g. \( \text{W}^{\text{VI}}\text{O}_6\text{(PO}_4\text{)}_{30}^{2-} \) with hetero-metals and used mass spectrometry to observe the presence of these species before isolating and characterising the compounds.

**Experimental approach: Discovery of the compounds using CSI-MS**

In our approach we aimed to replace the hetero-anion templates in the classical Dawson-like clusters e.g. \( \text{W}^{\text{VI}}\text{O}_6\text{(PO}_4\text{)}_{30}^{2-} \) with hetero-metals; by scanning the reaction mixtures before crystallisation we were able to locate the reaction systems that produced the \( \text{V}_2\text{[M}_n\text{V}_1] \) species. This was performed by precipitating solid from the various reaction systems under aqueous conditions. The precipitates were then transferred into the organic phase by ion exchange with tetrabutyl ammonium (TBA) and examined using mass spectrometry. Note: It is possible to examine the aqueous solution reactions directly but this often results in the observation of a plethora of species resulting from the multitude of possibilities arising from the clusters transferring with sodium and potassium cations with multiple water ligands. Therefore, ion exchange and phase transfer to organic solvent enables the individual cluster species to be assigned directly. The combination of solution control (adjustment of solution in terms of pH, metal ion concentrations, temperature and pressure) allows the direct observation of the species present in the reaction system with cryospray (CSI) mass spectrometry; an approach that we have recently found useful to observe reactive building blocks\(^{28}\) and high nuclearity clusters.\(^{39}\)

In this context we are utilising ESI/CSI-MS as a powerful tool to observe the self assembly of new POM clusters with novel templates and architectures which would not be easily isolated without prior detailed knowledge of the clusters present in the reaction solutions.

**Synthesis and structure of compounds 1–4**

Once the new clusters of the form \( \text{V}_2\text{[M}_n\text{V}_1] \) were observed in solution using the mass spectrometry studies, we were then able to isolate and characterise two new\(^{40}\) isostructural anion cluster architectures based on W and Mo respectively and we used these as four salts: \( \text{(Na}_n\text{)}\text{[NH}_4\text{]}\text{[H}_2\text{VW}_4\text{O}_8\text{(VO}_4\text{)}]_2} \text{(I)}, \text{(nBu}_4\text{N} \text{[H}_2\text{VW}_4\text{O}_8\text{(VO}_4\text{)}]_2} \text{(II)} \) (1 and 2 have virtually identical cluster anions), and \( \text{(TEAH)}\text{[H}_2\text{VMo}_6\text{O}_4\text{(VO}_4\text{)}]_2} \text{(III)} \) and \( \text{(nBu}_4\text{N} \text{[H}_2\text{VMo}_6\text{O}_4\text{(VO}_4\text{)}]_2} \text{(IV)} \) (4). It is interesting to note that in all four cases, each of the \( \text{[M}_n\text{V}_1] \) cluster anions contains two \( \text{[V}_0\text{O}_4\text{]}\text{vanadate templates} with one \( \text{[V}_0\text{O}_4\text{]}\text{vanadyl group} integrated into the \( \text{[M}_n\text{]} \) cluster framework (see Fig. 3).
The synthetic approach presented utilises Na2MoO4·2H2O (M: Mo or W) and NH4VO3 as the metal ion sources in aqueous medium with the presence of protonated triethanolamine (TEAH+) as a structure directing or ‘shrink-wrapping’ cation26,40 for the compound 3 and NH2OH·HCl for 1 under a variety of experimental conditions (hydrothermal process in the case of 1 and strict pH control under reflux for 3) to produce compounds 1/2 and 3/4 in relatively high yields (see Table 1). The use of a variety of experimental conditions proved to be of vital importance in such diverse systems as POMs. Furthermore, the compounds were characterized by elemental analysis, IR, UV-Vis, TGA studies as well as REDOX titrations (which demonstrate each compound is one electron reduced), solution ESI mass spectrometry, magnetic susceptibility, and single crystal XRD analysis (Tables 2–4). As reported below in a detailed discussion, a perfect agreement was established between the experimental techniques used in our efforts to discover the new species observed in the solution and thereafter to prove unambiguously the existence of an extra VIV metal centre on the shell of the Wells–Dawson structure.

The cluster anions α-[H4VW17O54(VO4)2]6− and α-[H3VMo17O54(VO4)2]6− determined crystallographically in 1/2, and 3/4, exhibit the distinctive Dawson-like cigar shape (if the

Table 3  Crystallographic data collection, intensity measurements and structure refinement parameters for compounds 1–4

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>H25N2O6Na4W11V1</td>
<td>C30H34N2W11V1O52</td>
<td>C30H34Mo17N6O88V3</td>
<td>C36H114Mo17N6O88V3</td>
</tr>
<tr>
<td>M/g mol−1</td>
<td>4616.52</td>
<td>5850.2</td>
<td>4355.73</td>
<td>102.154(2)</td>
</tr>
<tr>
<td>Symmetry</td>
<td>Trigonal</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>P21/c</td>
</tr>
<tr>
<td>Space group</td>
<td>R3−m</td>
<td>P 21/c</td>
<td>P 1</td>
<td></td>
</tr>
<tr>
<td>a/Å</td>
<td>37.655(3)</td>
<td>31.428(3)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>b/Å</td>
<td>37.655(3)</td>
<td>15.983(17)</td>
<td>102.154(2)</td>
<td>102.154(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>13.000(1)</td>
<td>33.615(4)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>α/</td>
<td>90.00</td>
<td>90.00</td>
<td>91.719(6)</td>
<td>91.012(6)</td>
</tr>
<tr>
<td>β/</td>
<td>90.00</td>
<td>102.154(2)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>γ/</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>V/Å3</td>
<td>15965(2)</td>
<td>16507.4(3)</td>
<td>4355.73</td>
<td>31.2232(11)</td>
</tr>
<tr>
<td>Z</td>
<td>9</td>
<td>4</td>
<td>31.2232(11)</td>
<td>15.8592(5)</td>
</tr>
<tr>
<td>μ/μm−1</td>
<td>27.947</td>
<td>12.026</td>
<td>106.848(6)</td>
<td>106.848(6)</td>
</tr>
<tr>
<td>F(000)</td>
<td>18099</td>
<td>10900</td>
<td>16064(6)</td>
<td>16215.5(10)</td>
</tr>
<tr>
<td>Crystal size/mm</td>
<td>0.18 × 0.12 × 0.03</td>
<td>0.26 × 0.09 × 0.03</td>
<td>0.18 × 0.15 × 0.10</td>
<td>0.18 × 0.10 × 0.06</td>
</tr>
<tr>
<td>No. data measured</td>
<td>122459</td>
<td>30657</td>
<td>44457</td>
<td>70889</td>
</tr>
<tr>
<td>No. unique data</td>
<td>1582</td>
<td>3670</td>
<td>18598</td>
<td>22223</td>
</tr>
<tr>
<td>RI</td>
<td>0.0443</td>
<td>0.0491</td>
<td>0.0567</td>
<td>0.1112</td>
</tr>
<tr>
<td>wR2 (all data)</td>
<td>0.1163</td>
<td>0.1057</td>
<td>0.1705</td>
<td>0.2913</td>
</tr>
<tr>
<td>Goodness of fit, S</td>
<td>1.160</td>
<td>1.018</td>
<td>0.946</td>
<td>1.057</td>
</tr>
</tbody>
</table>
framework V" ion is considered to be uniformly disordered over the entire framework) with an overall approximate D₃h symmetry, with a mirror plane dividing the cage into two equal parts linked together by six equatorial oxo ligands (Fig. 3 and 4). The cluster capsule-like shape is similar to that for \{M₈\} cages in the Dawson-like anions which incorporate heteroatoms of pyramidal geometry for example [H₄W₁₈O₆₅(OH)₄][P₄O₁₀]²⁻ and [H₄W₁₈O₆₅(AsO₃)²][W₁₈O₅₄XO₄]²⁻. Furthermore, the W–O framework of 1a, as well as the α-type coordination of the encapsulated atoms within the cage, is the same as that of a conventional Dawson [W₁₈O₅₄(XO₄)²]⁻ (X = SIV, SiIV, PIV) species previously reported, as well as in [Mo₁₈O₅₄(P₂O₇)²][W₁₈O₅₄(XO₄)²]. While the two central V" templates can be unambiguously located crystallographically, the 3rd vanadium (VIV) centre is disordered over the entire cluster framework with other 17 M centres. Fig. 4 shows the top \{M₈VIVVV\} section of the clusters 1–2 highlighting the three ‘capping’ and six ‘belt’ atom positions. For the \{W₁₈V₃\} cluster the terminal oxo ligands lie in the range 1.67–1.71 Å whereas in the \{Mo₁₈V₃\} these values range from 1.65–1.71 Å and we also suggest tentatively that the V" ion may be located in the ‘cap’ region due to the need to accommodate the long O–V bond trans to the terminal V=O group.

![Fig. 4](image)

### Cluster discovery and formula assignment: Protonation and redox state

The assignment of the formula for the clusters 1–4 is confirmed by elemental analysis (C/H/N/Mo/W/V), bond valence sum calculations, UV-vis spectroscopy, and, crucially, by CSI mass spectrometry.

During the course of this study, CSI-MS studies have proved to be a powerful tool in our effort to unveiling this unique family of clusters in solution prior to their structural analysis.

Importantly MS studies of the TBA salts of the \{M₈V₃\} dissolved in acetonitrile (M = W (2); Mo (4)) showed that the clusters are stable in solution. A range of charge (−3 to −5) and protonation (0–2) states were observed. Also the direct observation of \{(TBA)₈[W₁₈V₃O₆₂]\}²⁺ allows us to confirm that the clusters observed in the solid state which all have six cations associated, are protonated two-fold. This observation is extremely important since this gives unambiguous proof that the Dawson-capsules are present in solution, establishes the existence of a vanadium metal centre on the shell of the Dawson framework (which is almost impossible to distinguish crystallographically), and also confirms the extent of protonation of the cluster (in combination with X-ray, redox titrations and elemental analysis) which is extremely difficult to determine directly.

Also, to the best of our knowledge, compounds 1/2 and 3/4 represent the first example of the tungsten V-encapsulated polyoxoanion with a \{M₈V₃\} structure. The assignment of the clusters containing three vanadium ions is unambiguous, but it is nevertheless intriguing that precisely one vanadium ion is incorporated into the cluster framework. Note that the incorporation of the additional vanadium allows the cluster to be two-fold protonated and one possible explanation is that this helps stabilise the overall cluster type with the \{VO₄\}₃⁻ tetrahedral templates. In addition, preliminary synthetic studies with lower V: W ratios do not result in the isolation of the \{M₈V₃\} species, but only in lower yields of \{M₈V₂\} based product. This observation is interesting since recently the synthesis of a \{M₈V₂\} based species, \{Mo₁₈O₅₄(VO₄)\}²⁺ was reported. However, although we could directly observe small amounts of this species using mass spectrometry, attempts to synthesise this material using the approach given by Liu et al. result in the isolation of the \{Mo₁₈V₂\} compound described here.

### Magnetism

Susceptibility measurements between 2 and 290 K (0.1 T) indicate the presence of a single, uncoupled s = 1/2 vanadyl group per cluster unit. The product \(\chi T\) remains constant (0.37 emuK mol⁻¹, corresponding to \(g = 1.99\)) over the entire probed temperature range. In addition, magnetization measurements at 2.0 K as a function of an external field (0.1 to 5.0 T) produce a Brillouin function for a single s = 1/2 center.

### Redox titrations

Redox titrations carried out in aqueous medium utilizing 0.01 M Ce⁴⁺ solution as the oxidizing agent, for compounds 1 and 3 in order to clarify the extend of the reduction which took place under the reaction conditions. 4.8 and 6.1 mL (Table 4) of Ce⁴⁺

### Table 4 Consumed mL of Ce⁴⁺ solution and extended reduction for compounds 1 and 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>mL of Ce⁴⁺ used</th>
<th>Theoretical value for 1 e⁻ reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Na)₅(NH₄)₃[H₁V₁₇Wₙ₋₂O₆₄(VO₄)₃] 1</td>
<td>4.78</td>
<td>4.33</td>
</tr>
<tr>
<td>(TEAH)₅[H₁V₃Mo₇O₆₄(VO₄)₃] 3</td>
<td>5.90</td>
<td>5.23</td>
</tr>
</tbody>
</table>
were consumed to oxidize the compounds 1 and 3 completely establishing the one electron reduced form of the latter ones which is in agreement with the CSI studies. (For more details see the ES†).

**DFT studies**

Open-shell DFT calculations on the \( \{\text{H}_2\text{M}_i\text{V}_j\} \) cluster anion (1a, 3a) structures derived from anions of compounds 1 and 3, in which a single metal position of the \( \{\text{M}_i\text{O}_a\} \) shell was defined as vanadium, help us postulate the position of the \( \text{V}^\text{v} \) ion. The total energy favours the isomer with \( \text{V} \) localised in the two outer \( \text{M}_i \) cap groups over the other possible isomer with \( \text{V} \) as part of the two central \( \text{M}_i \) belt groups for both the molybdic (\( \Delta E = 12.3 \text{ kJ mol}^{-1} \)) and the tungstic (\( \Delta E = 10.7 \text{ kJ mol}^{-1} \)) anion, this difference is likely due to the absence of suitable ligand groups positioned \textit{trans} to the vanadyl groups in the belt-substituted isomer. Analysis of the single-occupied, highest molecular orbital shows that the single unpaired electron is localized virtually only on the cluster shell vanadyl group and not on the central \( \text{VO}_4 \) templates, so that we can formally assign the central \( \text{V} \) positions as \( \text{V}^\text{v} \) (in agreement with BVS calculations). However, the lowest unoccupied MOs see varying contributions from \( \text{Mo}(4d) \) and \( \text{W}(5d) \) components that reflect the colour differences of compounds 1 and 3 (predominantly due to IVCT transitions). Relative basicity studies reveal that the six \( \mu\text{-O} \) positions linking the two central \( \text{V} \) centres to the \( \text{Mo}/\text{W} \) belt positions are the most basic \( \text{O} \) positions in each cluster and are therefore most likely the sites of the two-fold protonation.

**Conclusions**

In conclusion, the discovery of the mixed-metal (\( \text{V}/\text{Mo} \) and \( \text{V}/\text{W} \)) Dawson-like capsules with the unique composition \( \{\text{M}_i\text{V}_j\} \) is reported. The compounds were firstly discovered in solution using cryospray mass spectrometry and then isolated as crystals. The strategy to use hydrothermal conditions to generate the tungsten analogue has proved to be successful in the case of 1, while the \textit{in-situ} formation and stability of both \( \text{V}/\text{Mo} \) and \( \text{V}/\text{W} \) Dawson capsules can be monitored by electrospray mass spectrometry. MS studies proved to be crucial in terms of establishing the existence of vanadium-based tetrahedral templates within the Dawson-like shell as well as the vanadium ion disorder over the cage framework. In future work we will exploit the approach outlined here in more detail—using DFT calculations and magnetic/ESR studies, while tracing self-assembly steps \textit{via} mass spectrometry, as well as in the solid state, to help design and unveil new members of this family of capsule compounds and study in more detail their catalytic and magnetic properties in relevance to their structural features.

**Experimental**

**General procedures**

All reagents and chemicals were purchased from commercial sources and used without further purification. Infrared spectra were recorded as KBr discs using a Perkin-Elmer paragon 1000 PC or Nicolet Magna 550 series II FTIR spectrometer.

### Synthetic procedures

**Synthesis of 1**: (\( \text{Na}_4 \text{NH}_3 \text{a}-[\text{H}_2 \text{VMo}_{17} \text{O}_{54} \text{VO}_2]_a \))

\( \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} \) (1.36 g, 4.1 mmol) and \( \text{NH}_2\text{OH-HCl} \) (1.3 g, 18.8 mmol) were dissolved in water (10 mL). Upon addition of \( \text{NH}_2\text{OH-HCl} \), precipitation of white solid occurred almost immediately. The solution stirred for 2 min and addition of \( \text{NH}_2\text{VO}_2 \) (0.2 g, 1.7 mmol) followed. Hydrochloric acid (37%, ~3 mL) was added to the stirred solution and the pH value of the solution was adjusted to 4. The mixture closed in an autoclave bomb, heated up to 160 °C for 3 days and cooled down slowly within one day. Dark brown block crystals suitable for X-ray crystal analysis were collected, washed with the minimum amount of cold ethanol and dried in air. The same material can be synthesized at pH values of 1, 2, and 3 as well but in lower yield. (Yield 0.89 g, 80%). IR bands (KBr): 3434, 1625 (\( \text{H}_2\text{O} \)), 957 (\( \text{V}^\text{O} \)), 891, 856, 760 (\( \text{O}-\text{M}-\text{O} \)) cm\(^{-1}\); UV-Vis (\( \text{H}_2\text{O} \)): 245 (15 320), 310 (11 566), 550 (368), nm (dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)). TGA: percentage weight loss (temperature (°C)): 4.67 (160, assigned to \( \text{H}_2\text{O} \)), 0.73 (208, assigned to \( \text{NH}_3 \)); Elemental analysis (%) calcd for \( \text{H}_2\text{Na}_4\text{Mo}_9\text{W}_{17}\text{O}_{54}\text{V}_2\text{O}_2 \): H 0.69, N 0.60, Na 1.99 V 3.31, W 67.70; found: H 0.60, N 0.69, Na 2.10, V 3.40, W 68.12.

**Synthesis of 2**: (\( \text{Na}_4\text{NH}_3\text{a}-[\text{H}_2 \text{VW}_{17} \text{O}_{54} \text{VO}_2]_a \))

Crystals of \( \text{Na}_4\text{NH}_3\text{a}-[\text{H}_2 \text{VW}_{17} \text{O}_{54} \text{VO}_2]_a \) were dissolved in the minimum amount of distilled \( \text{H}_2\text{O} \) (10 mL) and a solution of (\( \text{C}_2\text{H}_5\text{OH} \))\(\text{NBr}\) (2.0 g, 6.1 mmol) in water (25 mL) was added. A dark purple precipitate was collected by centrifuging, washed with water (3 × 20 mL) and ethanol (1 × 10 mL), and dried under vacuum. Recrystallization of the solid from acetonitrile solution with vapour diffusion of ether into the mother liquor afforded dark purple crystals of 2 the following day (yield 1.10 g, 60%). IR bands (KBr): 3434, 1625 (\( \text{H}_2\text{O} \)), 957 (\( \text{V}^\text{O} \)), 891, 856, 760 (\( \text{O}-\text{M}-\text{O} \)) cm\(^{-1}\); UV-Vis (\( \text{CH}_3\text{CN} \)): 238 (16 390), 298 (12 170), 526 (440), 657 (320) nm (dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)). TGA: percentage weight loss (temperature (°C)): 2.1 (265, assigned to \( \text{CH}_3\text{CN} \)), 24.85 (up to 800 °C, assigned to \( \text{Bu}_2\text{N}^+ \)); Elemental analysis (%) calcd for \( \text{C}_2\text{H}_5\text{Na}_4\text{N}_4\text{V}_3\text{W}_{17}\text{O}_{54} \): C 24.85, H 3.69, N 1.43, V 2.62, W 53.41; found: C 24.18, H 3.75, N 1.41, V 2.60, W 53.69. Positive mode CSIMS at 20 °C in \( \text{CH}_3\text{CN} \) \{\( \text{TBA}\)\(\text{H}_2\text{VW}_{17}\text{O}_{54}\)\(\text{V}_2\text{O}_2\)\(\text{a}\)\} \(\text{a}\) where \( n = 2 \) gives an envelope centred at \( m/z \) ca. 3106 and where \( n = 1 \) an envelope centred at \( m/z \) ca. 3227 as confirmed by isotopic fitting of the envelopes. Redox titration indicates that the compound is 1 electron reduced (see ES†).

**Synthesis of 3**: (\( \text{TEAH}_2\text{a}-[\text{H}_2 \text{VMo}_{17} \text{O}_{54} \text{VO}_2]_a \))

\( \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} \) (1.3 g, 4.1 mmol) and \( \text{TEAH} \) (1.3 g, 7.0 mmol) were dissolved in water (10 mL). Upon addition of TEAH, precipitation of white solid occurred almost immediately which redissolved gradually. The solution was stirred for 2 min followed by the addition of \( \text{NH}_2\text{VO}_2 \) (0.2 g, 1.7 mmol). Hydrochloric acid (37%, ~3 mL) was added to the stirred orange solution and the pH value was adjusted to 1. The mixture refluxed overnight and cooled down slowly within one day. Dark green block crystals suitable for X-ray crystal analysis were formed upon slow cooling to room temperature, collected by filtration, washed with the minimum
amount of cold ethanol and dried in air (yield 0.75 g, 85%).

IR bands (KBr): 3439, 1621 (H2O), 969 (V=O), 939 (Mo=O), 897, 861, 758 (O–M–O) cm⁻¹; UV-Vis (H2O): 243 (21 106), 308 (16 876), 587 (532) nm (dm³ mol⁻¹ cm⁻¹); TGA: percentage weight loss (temperature (°C)): 3.76 (170, assigned to H2O), 23.56 (up to 800 °C, assigned to TEAH⁺ cations); Elemental analysis (%) calcd for C36H96N6Mo17V3O80: C 11.33, H 2.51, N 2.20, V 4.00, Mo 42.55; found: C 11.25, H 2.61, N 2.19, V 4.10, Mo 42.55.

Synthesis of 4: ([TBA]6H2Mo17V3O62)

Crystals of (TEAH)6H2Mo17V3O62·8H2O (1.5 g, 0.39 mmol) were dissolved in the minimum amount of distilled H2O (10 mL) and a solution of (C4H9)4NBr (2.0 g, 6.1 mmol) in water (25 mL) was added. A dark green precipitate was collected by centrifuging, washed with water (3 × 20 mL) and cold ethanol (1 × 10 mL), and dried under vacuum. Recrystallization of the solid from acetonitrile solution with vapour diffusion of ether into mother liquor afforded dark green crystals of 4 the following day (yield 1.24 g, 75%). IR bands (KBr): 3439, 1621 (H2O), 969 (V=O), 942 (Mo=O), 891, 856, 760 (O–M–O) cm⁻¹; UV-Vis (CH3CN): 238 (18 906), 298 (14 666), 578 (693) nm (dm³ mol⁻¹ cm⁻¹); TGA: percentage weight loss (temperature (°C)): 2.88 (252, assigned to CH3CN), 33.48 (up to 800 °C, assigned to Bu₄N⁺); Elemental analysis (%) calcd for C36H96N6Mo17V3O80: C 11.33, H 2.51, N 2.20, V 4.00, Mo 42.55; found: C 11.25, H 2.61, N 2.19, V 4.10, Mo 42.55.

Crystallographic structure determinations

Details of data collection procedures and structure refinements are given in Table 3. Single crystals of suitable size were attached to glass fibres using Fomblin YR-1800 oil, and mounted. Some samples suffered solvent loss, and were glued to the glass fibre under solvent and transferred as rapidly as possible to the cold stream of the Oxford Instruments Cryostream. All data were collected on an Oxford Gemini CCD or Bruker Apex II CCD diffractometer, equipped with graphite monochromated X-radiation (λ = 0.71073 Å), running under the Collect software. The structures were solved by SHELXS-97. Most of the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were fixed with C–H = 0.96 Å, and were refined with a riding model and with Uiso set to 1.2 times that of the attached C atom. Refinement was with SHELXL-97 using full-matrix least-squares on F² and all the unique data. All samples showed the presence of disordered solvent molecules. All calculations were carried out using the WinGX package of crystallographic programs.

Density functional theory studies

Density functional theory calculations were performed using Turbomole 5.9.1 and Jaguar 7.0 on cluster ions in a surrounding field of +1 point charges. TZVP basis sets and B3-LYP hybrid functionals (for final single-point calculations) were used. The model structures were derived from crystallographic sets and were relaxed freely (employing B–P functionals), whereby a doming shift of the V positions out of the μ-O₃ plane towards the outer oxo position was observed as expected for a vanadyl group.

Cryospray mass spectroscopic measurements

CSI measurements were made at 20 °C (see Fig. 5 and 6). The solution of the sample was diluted so that the maximum concentration of the cluster ions was of the order of 10⁻⁵ M and this was infused into the electrospray at 180 μL h⁻¹. The mass spectrometer used for the measurements was a Bruker microTOFQ and the data were collected in both positive and

![Fig. 5](image-url) Positive ion mass spectrum showing the \{(TBA)₃n[H₄V₅W₅O₄₀]⁻\}⁺ in acetonitrile solution. Left: where n = 2 at m/z ca. 3106; Right: where n = 1 m/z ca. 3227. The blue line shows the actual spectrum and the red bar graph is the predicted envelope.
negative ion modes. The spectrometer was previously calibrated with the standard tune mix to give a precision of ca. 1.5 ppm in the region of 500–5000 m/z. The standard parameters for a medium mass data acquisition were used and the end plate voltage was set to −500 V and the capillary to +4500 V. The collision cell was set to a collision energy of 220 eV and the capillary to +4500 V. The collision cell was set to a collision energy of 220 eV. The predicted spectrum is calculated using Bruker Data Analysis 3.4 and is performed by calculating the predicted distribution of the cluster anion. In Fig. 6, the spectrum is shown between 2345 and 2370 m/z. The standard parameters for a medium collision cell were set to a collision energy of 220 eV. The predicted spectrum is calculated using Bruker Data Analysis 3.4 and is performed by calculating the predicted distribution of the cluster anion. In Fig. 6, the spectrum is shown between 2345 and 2370 m/z.

Fig. 6 Positive ion mass spectrum in acetonitrile solution of \{[\text{TBA}]_3[H_2V_{12}Mo_9O_{34}]\}^{2-}. Two envelopes can be seen where \( n = 3 \) (with all three V ions reduced to \( V^{2+} \) requiring 4 protons) gives an envelope centred at \( m/z \) ca. 2359 and where \( n = 1 \) (with 1 V ion reduced to \( V^{2+} \) requiring 1 proton) gives an envelope centred at \( m/z \) ca. 2358 as confirmed by isotopic fitting of the envelopes to the bifurcated isotopic distribution shown between 2345 and 2370 m/z range.

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Notes and references


