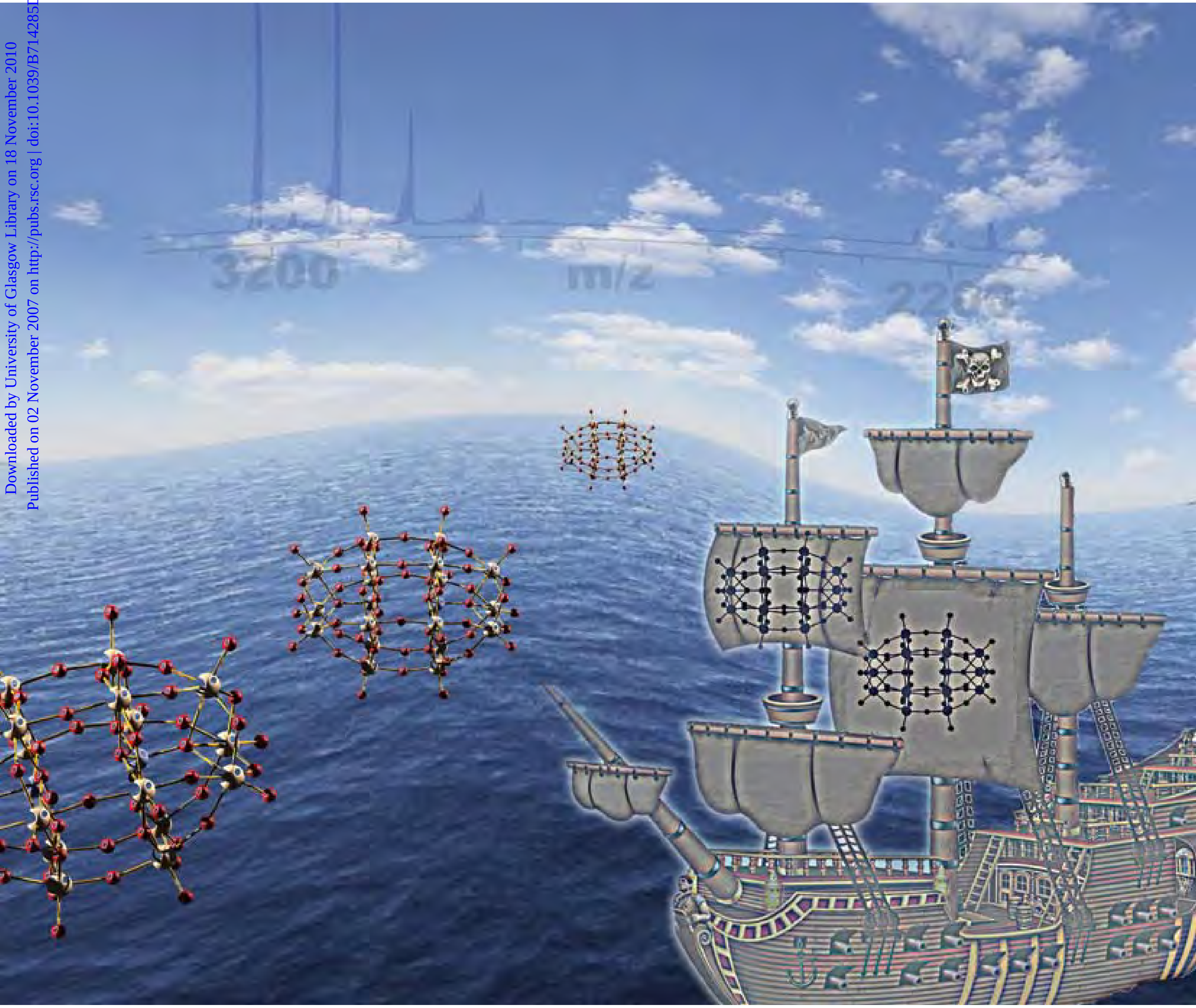
Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton

Number 2 | 14 January 2008 | Pages 173–304



ISSN 1477-9226

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1477-9226(2008)2;1-0

Bridging the gap between solution and solid state studies in polyoxometalate chemistry: Discovery of a family of $[V_1M_{17}]$-based cages encapsulating two $\{V^VO_4\}$ moieties†‡

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Received 17th September 2007, Accepted 3rd October 2007
First published as an Advance Article on the web 2nd November 2007
DOI: 10.1039/b714285d

A family of polyoxometalates with the composition $[H_2V_3M_{17}O_{62}]^{6-}$ features a Dawson-like architecture containing two tetrahedral $\{V^VO_4\}$ templates rather than main group hetero-anions ($\{PO_4\}$ or $\{SO_4\}$ *etc.*) typically associated with classical heteropolyacids, situated within a mixed-metal $\{M^{VI}{}_{17}V^{IV}O_{54}\}$ 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.[3] 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.[1,4] 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.[1,4] In particular the highly acidic properties of the highly stable Keggin-type heteropolyanions (HPAs)[8] such as $[W_{12}O_{36}(PO_4)]^{3-}$ or the atom transfer[20] of vanadium-substituted polyoxoanions such as $[H_2V_2Mo_{10}O_{36}(PO_4)]^{3-}$ render polyoxometalates as functional cluster systems.[3,21] 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.[8,22] 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 homometalic heteropolyanions with unequivalent d^0 metal atoms can be localized on preferential sites.[23,24] The development of high sensitivity methods for the direct and controllable synthesis and characterization leading to well-defined mixed cluster architectures[25,26] 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,[27,28] 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.[1,5–7] Therefore, the manipulation of some of the many reaction parameters often represents a straight-forward, 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.[19] 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

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† CCDC reference numbers 654676–654678 and 661130 for the structures **1**–**4**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714285d

‡ Electronic supplementary information (ESI) available: Details and graphs describing the REDOX titrations. See DOI: 10.1039/b714285d

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 W- and Mo-based cluster systems are guided by the fact that structures of polyoxomolybdate clusters are frequently derived from highly stable, low-nuclearity structural archetypes such as the O_h-symmetric Lindqvist[34] anion $[Mo_6O_{19}]^{2-}$ and the various isomers of the Keggin structure,[35] $[M_{12}O_{36}(XO_4)]^{n-}$, or the Dawson structure,[36] $[M_{18}O_{46}(XO_4)_2]^{n-}$ (X = S, P, As, Si *etc.*) (M = W, Mo).[37] Previously, by using protonated hexamethylenetetramine (HMTAH$^+$) as counter ions, we were able to stabilize and isolate a highly charged polyoxomolybdate anion, $[H_2Mo^{V}{}_4Mo^{VI}{}_{16}O_{52}]^{10-}$, $\{Mo_{16}\}$.[29,30]

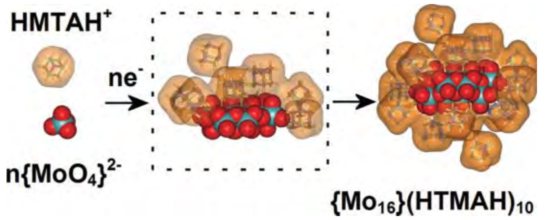

Fig. 1 A schematic showing the 'encapsulation' of the $[H_2Mo_{16}O_{52}]^{10-}$ cluster units during the cluster assembly process in the presence of the bulky organo-cation HMTA (hexamethylenetetramine).

In an extension to this approach we also recently isolated a family of sulfite-based Dawson-type mixed-valence polyoxomolybdates $[Mo_{18}O_{54}(SO_3)_2]^{n-}$, 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[29,30] or physical[31] features.

Herein, we present our very recent efforts, expand our approach to the isolation of new cluster types using 'encapsulating' and structure 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 $V_2{\subset}\{M_{17}V_1\}$ which have the α-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.* $[W^{VI}{}_{18}O_{54}(PO_4)_2]^{6-}$ with hetero-metals and we used mass spectrometry to observe the presence of these species *before* isolating and characterising the compounds.

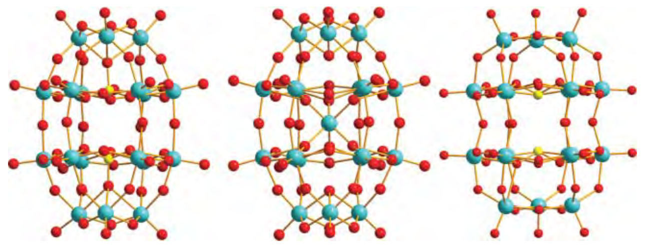

Fig. 2 Structural representation of α-$[W_{18}O_{54}(SO_4)_2]^{4-}$ cluster (left), the γ*-$[H_4W_{19}O_{62}]^{6-}$ cluster (middle) and the α-$[W_{18}O_{54}(SO_3)_2]^{4-}$ (right) for comparison of the different structures related to the Dawson archetype.[38] W: cyan; O: red; S: yellow.

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.* $[W^{VI}{}_{18}O_{54}(PO_4)_2]^{6-}$ with hetero-metals; by scanning the reaction mixtures before crystallisation we were able to locate the reaction systems that produced the $V_2{\subset}\{M_{17}V_1\}$ 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 reaction mixtures 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 $V_2{\subset}\{M_{17}V_1\}$ 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 isolated these as four salts: $(Na)_4(NH_4)_2$α-$[H_2VW_{17}O_{54}(VO_4)_2]$(**1**), $(nBu_4N)_6$α-$[H_2VW_{17}O_{54}(VO_4)_2]$ (**2**) (**1** and **2** have virtually identical cluster anions), and $(TEAH)_6$α-$[H_2VMo_{17}O_{54}(VO_4)_2]$ (**3**) and $(nBu_4N)_6$α-$[H_2VMo_{17}O_{54}(VO_4)_2]$ (**4**). It is interesting to note that in all four cases, each of the $\{M_{17}V_3\}$ cluster anions contains two $\{V^{V}O_4\}$ vanadate templates with one $\{V^{IV}O\}^{2+}$ vanadyl group integrated into the $\{M_{18}\}$ cluster framework (see Fig. 3).

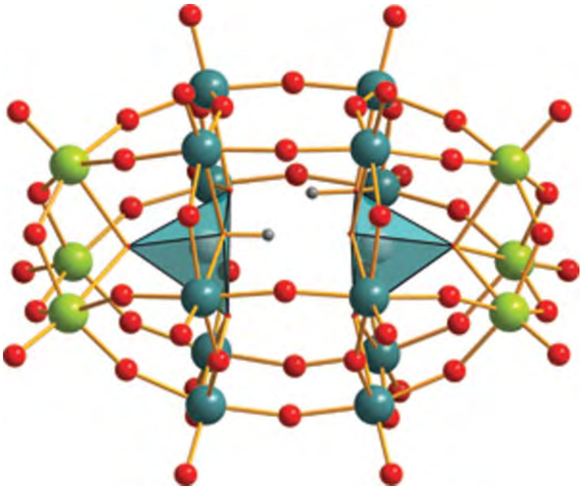

Fig. 3 Representations of the iso-structural frameworks found in the structures of compounds **1–4** (compound **1** is formally shown without counter ions or solvent) the general formula $[H_2VM_{17}O_{54}(VO_4)_2]^{6-}$ (M = W or Mo). The $\{M_{17}V_1\}$ framework shown in ball and stick and the V templates are shown by the polyhedra. Since the 'framework' V^{IV} ion can not be formally located, there are two structurally distinct positions over which it could be disordered; either over the six 'capping' M-sites shown by the light green spheres or over the twelve 'belt' positions shown by the dark green spheres. Colour scheme: Mo/W, green; O, red; V, cyan polyhedra; H, grey. The two protons are shown schematically but are of course disordered over the six inner μ_3 oxo ligands as suggested by structural arguments.

Table 1 Yields and codes of the obtained compounds

Compound	Yield	Code
$(Na)_4(NH_4)_2[H_2VW_{17}O_{54}(VO_4)_2]$	0.89 g, 80%	**1**
$(nBu_4N)_6[H_2VW_{17}O_{54}(VO_4)_2]$	1.10 g, 60%	**2**
$(TEAH)_6[H_2VMo_{17}O_{54}(VO_4)_2]$	0.75 g, 85%	**3**
$(nBu_4N)_6[H_2VMo_{17}O_{54}(VO_4)_2]$	1.24 g, 75%	**4**

The synthetic approach presented utilises $Na_2MO_4{\cdot}2H_2O$ (M: Mo or W) and NH_4VO_3 as the metal ion sources in aqueous medium with the presence of protonated triethanolamine ($TEAH^+$) as a structure directing or 'shrink-wrapping' cation[26,40] for the compound **3** and $NH_2OH{\cdot}HCl$ 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 V^{IV} metal centre on the shell of the Wells–Dawson structure.

The cluster anions α-$[H_2VW_{17}O_{54}(VO_4)_2]^{6-}$ **1a** and α-$[H_2VMo_{17}O_{54}(VO_4)_2]^{6-}$ **2a** determined crystallographically in **1**/**2**, and **3**/**4**, exhibit the distinctive Dawson-like cigar shape (if the

Table 2 Average bond distances [Å] and BVS values of the compounds **1–4**

Compound	$M{=}O_{av}$	$M{-}O_{av}$	$V_{template}{-}O_{av}$	M BVS_{av} (Mo, W)	$V_{template}$ BVS_{av}
1	1.67(1)	2.03(19)	1.74(2)	6.05	4.84
2	1.70(9)	2.00(15)	1.71(2)	6.01	5.07
3	1.67(2)	2.01(15)	1.73(2)	6.00	4.91
4	1.67(1)	2.00(14)	1.71(4)	5.99	5.10

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

	1	**2**	**3**	**4**
Chemical Formula	$H_{32}N_2O_{74}Na_4W_{17}V_3$	$C_{102}H_{227}N_9W_{17}V_3O_{62}$	$C_{36}H_{114}Mo_{17}N_6O_{88}V_3$	$C_{102}H_{227}N_9Mo_{17}V_3O_{62}$
$M/g\ mol^{-1}$	4616.52	5850.20	3823.13	4355.73
Symmetry	Trigonal	Monoclinic	Triclinic	Monoclinic
Space group	*R*3-*m*	*P* $2_1/c$	*P*-1	*P*$2_1/c$
a/Å	37.655(3)	31.428(3)	13.995(3)	31.2232(11)
b/Å	37.655(3)	15.9838(17)	16.060(4)	15.8592(5)
c/Å	13.000(1)	33.615(4)	24.086(6)	33.54755(14)
α/°	90.00	90.00	106.848(6)	90.00
β/°	90.00	102.154(2)	91.719(6)	102.542(4)
γ/°	120.00	90.00	91.012(6)	90.00
$V/Å^3$	15965(2)	16507.4(3)	5177(2)	16215.5(10)
Z	9	4	2	4
μ/mm^{-1}	27.947	12.026	2.359	1.507
F(000)	18099	10900	3718	8724
Crystal size/mm	0.18 × 0.15 × 0.10	0.26 × 0.09 × 0.03	0.18 × 0.15 × 0.10	0.18 × 0.10 × 0.06
No. data measured	1970	122459	44457	70889
No. unique data	1582	30657	18598	22223
$R1$	0.0443	0.0491	0.0567	0.1112
$wR2$ (all data)	0.1163	0.1057	0.1705	0.2913
Goodness of fit, S	1.160	1.018	0.946	1.057

Table 4 Consumed mL of Ce^{IV} solution and extended reduction for compounds **1** and **3**

Compound	mL of Ce^{IV} used	Theoretical value for 1 e^- reduction
$(Na)_4(NH_4)_2[H_2VW_{17}O_{54}(VO_4)_2]$ **1**	4.78	4.33
$(TEAH)_6[H_2VMo_{17}O_{54}(VO_4)_2]$ **3**	5.90	5.23

framework V^{IV} ion is considered to be uniformly disordered over the entire framework) with an overall approximate D_{3h} 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 $\{M_{18}\}$ cages in the Dawson-like anions which incorporate heteroatoms of pyramidal geometry for example $[H_2W_{18}O_{57}(BiO_3)]^{7-}$ and $[H_2W_{18}O_{57}(AsO_3)]^{7-}$.[41] 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 $[W_{18}O_{54}(XO_4)_2]^{n-}$ ($X = S^{VI}$, Si^{IV}, P^{V}) species previously reported, as well as in $[Mo_{18}O_{54}(P_2O_7)]^{4-}$.[42] While the two central V^{V} templates can be unambiguously located crystallographically, the 3rd vanadium (V^{IV}) centre is disordered over the entire cluster framework with other 17 M centres. Fig. 4 shows the top $\{M_8V^{IV}V^{V}\}$ section of the clusters **1–2** highlighting the three 'capping' and six 'belt' atom positions. For the $\{W_{17}V_3\}$ cluster the terminal oxo ligands lie in the range 1.67–1.71 Å whereas in the $\{Mo_{17}V_3\}$ these values range from 1.65–1.71 Å and we also suggest tentatively that the V^{IV} 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.

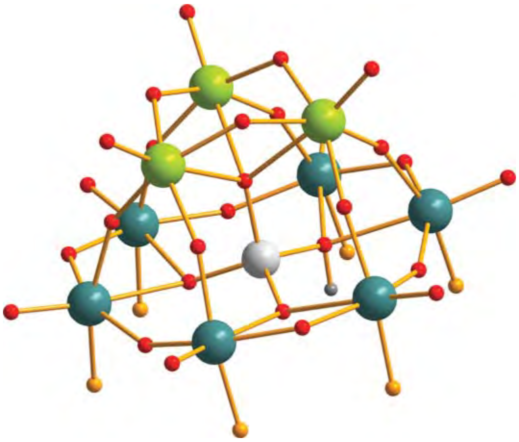

Fig. 4 Representation of the $\{M_8V^{IV}V^{V}\}$ section found in clusters **1–4**. The three 'capping' metal ion positions are shown in light green and the six 'belt' positions in dark green and the template V^{V} is shown in grey. The V^{IV} ion is disordered over the framework. The six bridging oxo ligands which link both halves of the cluster are shown in orange.

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 valance 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 $\{M_{17}V_3\}$ dissolved in acetonitrile (M = W (**2**); Mo (**4**)) showed that the clusters are stable in solution. A range of charge (−1 to −3) and protonation (0–2) states were observed. Also the direct observation of $\{(TBA)_8[H_2V_3W_{17}O_{62}]\}^{2+}$ 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 $\{M_{17}V_3\}$ 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 $\{VO_4\}$ tetrahedral templates. In addition, preliminary synthetic studies with lower V : W ratios do not result in the isolation of the $\{M_{18}V_2\}$ species, but only in lower yields of $\{M_{17}V_3\}$-based product. This observation is interesting since recently the synthesis of a $\{M_{18}V_2\}$ based species, $[Mo_{18}O_{54}(VO_4)_2]^{6-}$ was reported.[40] 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.*[40] result in the isolation of the $\{Mo_{17}V_3\}$ 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 χT 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 Ce^{IV} 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 Ce^{IV}

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 ESI‡).

DFT studies

Open-shell DFT calculations on the $\{H_2M_{17}V_3\}$ cluster anion (**1a**, **3a**) structures derived from anions of compounds **1** and **3**, in which a single metal position of the $\{M_{18}O_{54}\}$ shell was defined as vanadium, help us postulate the position of the V^{IV} ion: The total energy favours the isomer with V localised in the two outer M_3 cap groups over the other possible isomer with V as part of the two central M_6 belt groups for both the molybdate (ΔE = 12.3 kJ mol^{-1}) and the tungstate (ΔE = 10.7 kJ mol^{-1}) anion, this difference is likely due to the absence of suitable ligand groups positioned *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 VO_4 templates, so that we can formally assign the central V positions as V^V (in agreement with BVS calculations). However, the lowest unoccupied MOs see varying contributions from Mo(4d) and 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 μ-O positions linking the two central V centres to the Mo/W belt positions are the most basic 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 (V/Mo and V/W) Dawson-like capsules with the unique composition $\{M_{17}V_3\}$ is reported. The compounds were firstly discovered in solution using cryospray mass spectrometry and then isolated in high yields. The strategy to use hydrothermal conditions to generate the tungsten analogue has proved to be successful in the case of **1**, while the *in-situ* formation and stability of both V/Mo and V/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 approached outlined here in more detail—using DFT calculations and magnetic/ESR studies, while tracing self-assembly steps *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: $(Na)_4(NH_4)_2\alpha$-$[H_2VW_{17}O_{54}(VO_4)_2]$

$Na_2WO_4\cdot2H_2O$ (1.36 g, 4.1 mmol) and $NH_2OH\cdot HCl$ (1.3 g, 18.8 mmol) were dissolved in water (10 mL). Upon addition of $NH_2OH\cdot HCl$, precipitation of white solid occurred almost immediately. The solution stirred for 2 min and addition of NH_4VO_3 (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 (H_2O), 957 (V=O), 915 (W=O), 891, 856, 760 (O–M–O) cm^{-1}; UV-Vis (H_2O): 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 H_2O), 0.73 (208, assigned to NH_3); Elemental analysis (%) calcd for $H_{32}N_2O_{74}Na_4W_{17}V_3$: 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: $(nBu_4N)_6\alpha$-$[H_2VW_{17}O_{54}(VO_4)_2]$

Crystals of $Na_4(NH_4)_2H_2W_{17}V_3O_{62}\cdot12H_2O$ **1** (1.5 g, 0.32 mmol) were dissolved in the minimum amount of distilled H_2O (10 mL) and a solution of $(C_4H_9)_4NBr$ (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 (H_2O), 957 (V=O), 915 (W=O), 891, 856, 760 (O–M–O) cm^{-1}; UV-Vis (CH_3CN): 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 CH_3CN), 24.85 (up to 800 °C, assigned to Bu_4N^+); Elemental analysis (%) calcd for $C_{96}H_{216}N_6W_{17}V_3O_{62}$: 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 CH_3CN $\{(TBA)_{10-n}[H_nV_3W_{17}O_{62}]\}^{2+}$ 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 ESI‡).

Synthesis of 3: $(TEAH)_6\alpha$-$[H_2VMo_{17}O_{54}(VO_4)_2]$

$Na_2MoO_4\cdot2H_2O$ (1.3 g, 4.1 mmol) and TEA (1.3 g, 7.0 mmol) were dissolved in water (10 mL). Upon addition of TEA, precipitation of white solid occurred almost immediately which redissolved gradually. The solution was stirred for 2 min followed by the addition of NH_4VO_3 (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 (H_2O), 969 (V=O), 939 (Mo=O), 897, 861, 758 (O–M–O) cm^{-1}; UV-Vis (H_2O): 243 (21 106), 308 (16 876), 587 (532) nm ($dm^3\ mol^{-1}\ cm^{-1}$); TGA: percentage weight loss (temperature (°C)): 3.76 (170, assigned to H_2O), 23.56 (up to 800 °C, assigned to $TEAH^+$ cations); Elemental analysis (%) calcd for $C_{36}H_{96}N_6Mo_{17}V_3O_{80}$: C 11.33, H 2.51, N 2.20, V 4.00, Mo 42.63; found: C 11.25, H 2.61, N 2.19, V 4.10, Mo 42.55.

Synthesis of 4: $(n\mathrm{Bu}_4\mathrm{N})_6\alpha$-$[\mathrm{H}_2\mathrm{VMo}_{17}\mathrm{O}_{54}(\mathrm{VO}_4)_2]$

Crystals of $(TEAH)_6H_2Mo_{17}V_3O_{62}\cdot 8H_2O$ (1.5 g, 0.39 mmol) were dissolved in the minimum amount of distilled H_2O (10 mL) and a solution of $(C_4H_9)_4NBr$ (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): 3434, 1625 (H_2O), 965 (V=O), 942 (Mo=O), 891, 856, 760 (O–M–O) cm^{-1}; UV-Vis (CH_3CN): 238 (18 906), 298 (14 666), 578 (693) nm ($dm^3\ mol^{-1}\ cm^{-1}$); TGA: percentage weight loss (temperature (°C)): 2.88 (252, assigned to CH_3CN), 33.48 (up to 800 °C, assigned to Bu_4N^+); Elemental analysis (%) calcd for $C_{96}H_{216}N_6Mo_{17}V_3O_{62}$: C 26.45, H 4.95, N 1.93, V 3.51, Mo 37.42; found: C 26.94, H 5.10, N 2.01, V 3.60, Mo 37.99. Positive mode CSIMS at 20 °C in CH_3CN $\{(TBA)_8[H_{n+1}V^{V}{}_{3-n}V^{IV}{}_nMo_{17}O_{62}]\}^{2+}$ where $n = 3$ gives an envelope centred at *m*/*z ca.* 2359 and where $n = 1$ 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 mass units.

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 ($\lambda = 0.71073$ Å), running under the Collect software. The structures were solved by SHELXS-97.[43–47] 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 U_{iso} set to 1.2 times that of the attached C atom. Refinement was with SHELXL-97 using full-matrix least-squares on F^2 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.

CCDC reference numbers 654676–654678 and 661130 for the structures **1–4**.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714285d

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-O_4 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

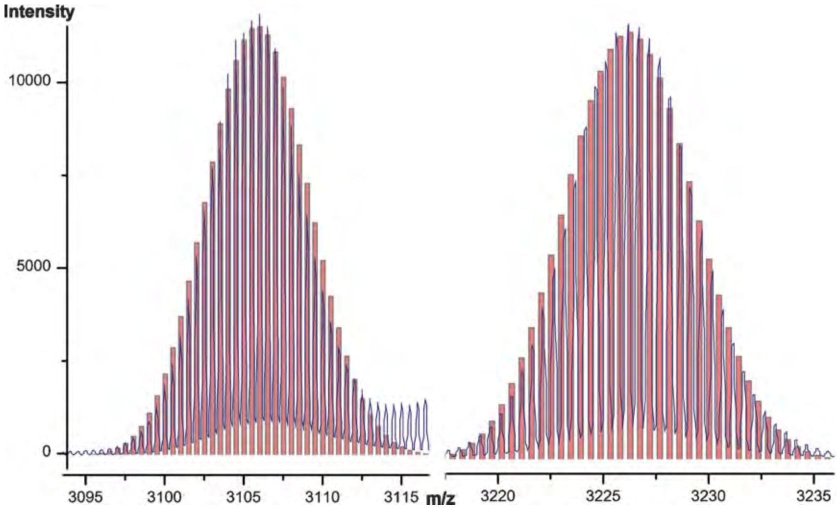

Fig. 5 Positive ion mass spectrum showing the $\{(TBA)_{10-n}[H_nV_3W_{17}O_{62}]\}^{2+}$ in acetonitrile solution. *Left*: where $n = 2$ at *m*/*z ca.* 3106; *Right*: where $n = 1$ *m*/*z ca.* 3227. The blue line shows the actual spectrum and the red bar graph is the predicted envelope.

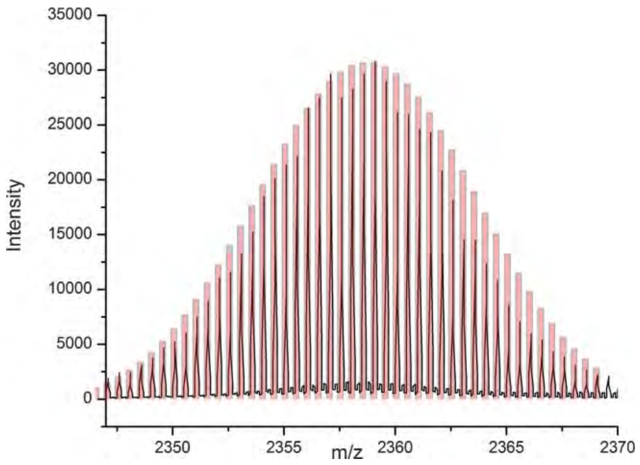

Fig. 6 Positive ion mass spectrum in acetonitrile solution of $\{(TBA)_8[H_{n+1}V^{V}_{3-n}V^{IV}_{n}Mo_{17}O_{62}]\}^{2+}$. Two envelopes can be seen where $n = 3$ (with all three V ions reduced to V^{IV} requiring 4 protons) gives an envelope centred at *m*/*z* *ca.* 2359 and where $n = 1$ (with 1 V ion reduced to V^{IV} 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.

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 −8.0 eV z^{-1} with a gas flow rate at 25% of maximum and the cell RF was set at 600 Vpp.

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 composed of $\{(TBA)_8[H_1V^{V}_3Mo^{VI}_{17}O_{62}]\}^{2+}$ and $\{(TBA)_8[H_4V^{IV}_3\text{-}Mo^{VI}_{17}O_{62}]\}^{2+}$ *i.e.* for the formula $C_{128}H_{289}N_8V_3Mo_{17}O_{62}$ and $C_{128}H_{292}N_8V_3Mo_{17}O_{62}$ which gives the formula weights for the dication of 2358.1/2359.61 compared to the observed *m*/*z* (100%) peak which appears at 2357.6/2359.1 respectively. The slight discrepancy between the fitted intensity and the expected arises since there is a non-equal population of the singly and tetra protonated species.

Acknowledgements

We thank the Royal Society, the EPSRC and the University of Glasgow for support and we thank Bruker Daltonics for collaboration using the microTOFQ and the cyrospray source.

Notes and references

1 D.-L. Long, E. Burkholder and L. Cronin, *Chem. Soc. Rev.*, 2007, **36**, 105; L. Cronin, *Comprehensive Coordination Chemistry II*, ed., J. A. McCleverty and T. J. Meyer, Elsevier, Amsterdam, 2004, vol. 7, p. 1.
2 B. Hasenknopf, *Front. Biosci.*, 2005, **10**, 275.
3 M. V. Vasylyev and R. Neumann, *J. Am. Chem. Soc.*, 2004, **126**, 884; I. M. Mbomekalle, B. Keita, L. Nadjo, P. Berthet, K. I. Hardcastle, C. L. Hill and T. M. Anderson, *Inorg. Chem.*, 2003, **42**, 1163.
4 M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34; C. L. Hill, *Chem. Rev.*, 1998, **98**, 1.
5 K. Wassermann, M. H. Dickman and M. T. Pope, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1445.
6 L. Cronin, C. Beugholt, E. Krickemeyer, M. Schmidtmann, H. Bögge, P. Kögerler, T. K. K. Luong and A. Müller, *Angew. Chem., Int. Ed.*, 2002, **41**, 2805.
7 A. Müller, E. Beckmann, H. Bögge, M. Schmidtmann and A. Dress, *Angew. Chem., Int. Ed.*, 2002, **41**, 1162.
8 I. V. Kozhevnikov, *Chem. Rev.*, 1998, **98**, 171.
9 J. T. Rhule, W. A. Neiwert, K. I. Hardcastle, B. T. Do and C. L. Hill, *J. Am. Chem. Soc.*, 2001, **123**, 12101.
10 A. Müller, M. Luban, C. Schröder, R. Modler, P. Kögerler, M. Axenovich, J. Schnack, P. Canfield, S. Bud'ko and N. Harrison, *ChemPhysChem*, 2001, **2**, 517.
11 A. Müller, P. Kögerler and A. W. M. Dress, *Coord. Chem. Rev.*, 2001, **222**, 193.
12 D. M. Way, A. M. Bond and A. G. Wedd, *Inorg. Chem.*, 1997, **36**, 2826.
13 P. J. S. Richardt, J. M. White, P. A. Tregloan, A. M. Bond and A. G. Wedd, *Can. J. Chem.*, 2001, **79**, 613.
14 K. F. Aguey-Zinsou, P. V. Bernhardt, U. Kappler and A. G. Mcewan, *J. Am. Chem. Soc.*, 2003, **125**, 530.
15 D. A. Judd, J. H. Nettles, N. Nevins, J. P. Snyder, D. C. Liotta, J. Tang, J. Ermolieff, R. F. Schinazi and C. L. Hill, *J. Am. Chem. Soc.*, 2001, **123**, 886.
16 H. D. Zeng, G. R. Newkome and C. L. Hill, *Angew. Chem., Int. Ed.*, 2000, **39**, 1772.
17 F. Ogliaro, S. P. de Visser, S. Cohen, P. K. Sharma and S. Shaik, *J. Am. Chem. Soc.*, 2002, **124**, 2806.
18 D.-L. Long, H. Abbas, P. Kögerler and L. Cronin, *Angew. Chem., Int. Ed.*, 2005, **44**, 3415.
19 P. Kögerler P and L. Cronin, *Angew. Chem., Int. Ed.*, 2005, **44**, 844.
20 R. Neumann and A. M. Khenkin, *Chem. Commun.*, 2006, 2529.
21 N. Mizuno, K. Yamaguchi and K. Kamata, *Coord. Chem. Rev.*, 2005, **249**, 1944.
22 L. Cronin, *Angew. Chem., Int. Ed.*, 2006, **45**, 3576.
23 M. Kozik, C. F. Hammer and L. C. W. Baker, *J. Am. Chem. Soc.*, 1986, **108**, 2748; D. C. Duncan and C. L. Hill, *Inorg. Chem.*, 1996, **35**, 5828; A. Teze, J. Canny, L. Gurban, R. Thouvenot and G. Herve, *Inorg. Chem.*, 1996, **35**, 1001.
24 B. Keita, E. Abdeljalil, L. Nadjo, R. Contant and R. Belgiche, *Electrochem. Commun.*, 2001, **3**, 56; M. Abbessi, K. M. Allal, M. Bendjaballah and M. E. Semar, *J. Soc. Alger. Chim.*, 1994, **4**, 1; B. Keita, E. Abdeljalil, L. Nadjo, B. Avisse, R. Contant, J. Canny and M. Richet, *Electrochem. Commun.*, 2002, **2**, 145.
25 D.-L. Long and L. Cronin, *Chem.–Eur. J.*, 2006, **12**, 3698.
26 D.-L. Long, P. Kögerler, L. J. Farrugia and L. Cronin, *Angew. Chem., Int. Ed.*, 2003, **42**, 4180; C. Ritchie, E. Burkholder, P. Kögerler and L. Cronin, *Dalton Trans.*, 2006, **14**, 1712.
27 L. Cronin, C. Beugholt, E. Krickemeyer, M. Schmidtmann, H. Bögge, P. Kögerler, T. K. K. Luong and A. Müller, *Angew. Chem., Int. Ed.*, 2002, **41**, 2805; B. Botar, P. Kögerler and C. L. Hill, *J. Am. Chem. Soc.*, 2006, **128**, 5336; K. Wassermann, M. H. Dickman and M. T. Pope, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1445.
28 C. Ritchie, E. M. Burkholder, D.-L. Long, D. Adam, P. Kögerler and L. Cronin, *Chem. Commun.*, 2007, 478.
29 D.-L. Long, P. Kögerler, L. J. Farrugia and L. Cronin, *Angew. Chem., Int. Ed.*, 2003, **42**, 4180.
30 D.-L. Long, P. Kogerler, L. J. Farrugia and L. Cronin, *Dalton Trans.*, 2005, 1372.
31 D.-L. Long, P. Kögerler and L. Cronin, *Angew. Chem., Int. Ed.*, 2004, **43**, 1817.
32 D.-L. Long, P. Kögerler, D. Orr, G. Seeber, L. J. Farrugia and L. Cronin, *J. Cluster Sci.*, 2003, **14**, 313; D.-L. Long, H. Abbas, P. Kögerler and L. Cronin, *J. Am. Chem. Soc.*, 2004, **126**, 13880.
33 H. Abbas, A. L. Pickering, D.-L. Long, P. Kögerler and L. Cronin, *Chem.–Eur. J.*, 2005, **11**, 1071.
34 D. Hagrman, P. J. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 3165; S. S. Kuduva, N. Avarvari and M. Fourmigue, *J. Chem. Soc., Dalton Trans.*, 2002, 3686.
35 P. Mialane, A. Dolbecq, L. Lisnard, A. Mallard, J. Marrot and F. Secheresse, *Angew. Chem., Int. Ed.*, 2002, **41**, 2398.
36 T. Hori, O. Tamada and S. Himeno, *J. Chem. Soc., Dalton Trans.*, 1989, 1491; S. Juraja, T. Vu, P. J. S. Richardt, A. M. Bond, T. J. Cardwell, J. D. Cashion, G. D. Fallon, G. Lazarev, B. Moubaraki, K. S. Murray and A. G. Wedd, *Inorg. Chem.*, 2002, **41**, 1072.

37 M. T. Pope, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 3, p. 1023.

38 B. Dawson, *Acta Crystallogr.*, 1953, **6**, 113; M. Holscher, U. Englert, B. Zibrowius and F. Holderich, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2491; H. Ichida and Y. Sasaki, *Acta Crystallogr., Sect. C*, 1983, **39**, 529; D. Long, P. Kogerler, A. D. C. Parenty, John Bielden and Leroy Cronin, *Angew. Chem., Int. Ed.*, 2006, **45**, 4798; D.-L. Long, H. Abbas, P. Kögerler and L. Cronin, *Angew. Chem., Int. Ed.*, 2005, **44**, 3415.

39 G. J. T. Cooper, G. N. Newton, P. Kögerler, D.-L. Long, L. Engelhardt, M. Luban and L. Cronin, *Angew. Chem., Int. Ed.*, 2007, **46**, 1340.

40 D.-D. Liang, S.-X. Liu, Y.-H. Ren, C.-D. Zhang and L. Xu, *Inorg. Chem. Commun.*, 2007, **10**, 933.

41 Y. Ozawa and Y. Sasaki, *Chem. Lett.*, 1987, 923; Y. Jeannin and J. Martin-Frere, *Inorg. Chem.*, 1979, **18**, 3010.

42 U. Kortz and M. T. Pope, *Inorg. Chem.*, 1994, **33**, 5643.

43 *SMART-NT Software Reference Manual*, version 5.059, Bruker AXS, Inc., Madison, WI, 1998.

44 *SAINT+ Software Reference Manual*, version 6.02, Bruker AXS, Inc., Madison, WI, 1999.

45 G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structure*, University of Göttingen, Germany, 1997.

46 G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, 1997.

47 *SHELXTL-NT Software Reference Manual*, version 5.1, Bruker AXS, Inc., Madison, WI, 1999.