Controlling transformations in the assembly of polyoxometalate clusters: {Mo$_{11}$V$_7$}, {Mo$_{17}$V$_8$} and {Mo$_{72}$V$_{30}$}†

Haralampos N. Miras, M. Nieves Corella Ochoa, De-Liang Long and Leroy Cronin*

The reaction of molybdate with vanadium(v) in the presence of sulfite anions is explored showing how, *via* cation control, stepwise assembly through the {Mo$_{11}$V$_7$} cluster yields a {M$_{25}$} cluster-based compound, [Mo$^{VI}_{11}$V$^V_5$V$^{IV}_2$O$_{52}$(μ$_9$-SO$_3$)(Mo$^{VI}_6$V^{V}O$_{22}$)]$^{10-}$ (1a), which was first discovered using cryospray mass spectrometry, whereas switching the cation away from ammonium allows the direct formation of the spherical 'Keplerate' {Mo$_{72}$V$_{30}$} cluster.

The 'one-pot' reaction approach to the formation of poly-oxometalate clusters (POMs), anionic oxide clusters of early transition metals (Mo, W, V, Nb),[1] can be frustrating since extremely small changes in reaction conditions can yield totally different results.[2] In an effort to gain control and direct the assembly process, different techniques have been employed such as the use of structure directing "shrink-wrapping" organic cations,[2] control of ionic strength,[3] reaction and crystallisation under continuous flow conditions,[4] and the direct observation of new clusters as they are formed using electrospray and cryospray mass spectrometry.[5] In hetero-polyanion chemistry, much of these reactions have been carried out utilising tetrahedral main group anions such as sulfate and phosphate,[6] however the use of the pyramidal sulfite anion can have a profound effect on the structure and functionality of the resulting cluster[7] allowing the assembly of clusters with a remarkable range of structures and properties.[8,9] This is because the C_{3v} symmetric sulfite anion contains a nonbonding, but stereochemically active lone pair of electrons which can help impart additional redox[9] and photophysical properties.[10] Herein we report the synthesis and isolation of a {M$_{25}$}={Mo$_{17}$V$_8$} cluster, which is related to a parent {M$_{18}$}={Mo$_{11}$V$_7$} cluster which itself is related to the {M$_{18}$} 'Dawson-like' cluster whereby seven of the metal centres have been replaced by V$^{V/IV}$ metal centres and a {Mo$_6$V} "crown" decorates the upper part of the Dawson-like structure to yield the largest sulfite based POM species (NH$_4$)$_{10}$[Mo$^{VI}_{11}$V$^V_5$V$^{IV}_2$O$_{52}$-(μ$_9$-SO$_3$)(Mo$^{VI}_6$V^{V}O$_{22}$)]·14H$_2$O **1**. Furthermore, this species was first observed in solution using CSI mass spectrometry, before isolation and structural elucidation using X-ray crystallography.‡

Generally, the design of new cluster systems which exhibit functionality is a major challenge in inorganic cluster chemistry, since this could potentially lead to the discovery and development of functional nanoscale materials built using a 'bottom-up' self-assembly approach.[11] In this respect we have been utilising mass spectrometry to 'scan' the reaction systems to help identify potentially novel and interesting cluster structural motifs in solution before 'discovery' by crystallisation. For example the sequential addition of solid NH$_4$V^{V}O$_3$ and (NH$_4$)$_2$SO$_3$ in an acidified aqueous (37% HCl in water, 1 : 4 v/v) solution of (NH$_4$)$_6$Mo$^{VI}_7$O$_{24}$ resulted in the formation of deep purple material, compound **1**, after adjustment of the experimental conditions such as metal to metal ratio and acidity.§ Based on our previous work, when we discovered the {Mo$_{11}$V$_7$} cluster, we used these reaction conditions as a starting point to 'screen' the experimental parameters and identify the {Mo$_{17}$V$_8$} cluster *via* ion exchange using mass spectrometry.

Subsequent crystallisation of **1** allowed the solid state characterisation, and at this point it is worth noting the interesting chemical information which has been transferred from the parent molecule: (a) the existence of the oxidized form of six vanadium centres in the presence of a reducing agent, even though the vanadium(v) at the beginning is reduced rapidly to vanadium(iv) by the sulfite anion;[8](b) a plethora of modes are adopted by the metal centres in the same structure as shown by the structural analysis (dioxo-/oxo-Mo^{VI} and octahedrally/tetrahedrally coordinated V$^{V/IV}$ centres).

Crystallographic studies revealed that **1** can be formulated as (NH$_4$)$_{10}$[Mo$^{VI}_{11}$V$^V_5$V$^{IV}_2$O$_{52}$(μ$_9$-SO$_3$)(Mo$^{VI}_6$V^{V}O$_{22}$)]·14H$_2$O whereby the anion **1a** adopts a "crowned"-Dawson like structure and consists of three parts. The distorted egg-shaped capsule of the molybdovanadate-sulfite anion is built up from two different hemispheres, being related to the parent cluster [Mo$^{VI}_{11}$V$^V_5$V$^{IV}_2$O$_{52}$(μ$_9$-SO$_3$)]$^{7-}$.[8e] As before, the lower part of **1a** consists of two hemispheres where three edge-sharing MoO$_6$ octahedra form the cap connected to the belt *via* vertices of alternating V^{V}O$_4$ tetrahedra and MoO$_6$ octahedra. The remaining four V positions (two V^V and two V^{IV}) are crystallographically disordered in the lower part of the cluster over nine potential positions, and the cavity is occupied by one sulfite anion since the tetrahedrally coordinated V metal centres cause the upper hemisphere to contract and diminish the available space; *i.e.* the V centres in **1a** are located only 4.751(2) Å away from each other, while in the classical Mo-based Dawson structure, the equivalent Mo centres lie 6.134(1) Å apart. In this case a "crown"-like fragment is attached to the three MoO$_6$ centres located at the top of the 'Dawson' cap through 6 oxo-bridges and consists of three pairs of corner shared MoO$_6$ units comprising two terminal oxo groups. The centre of the "crown" is occupied by a tetrahedrally coordinated vanadium(v) centre (Fig. 1). One important structural aspect is the presence of the μ$_9$-SO$_3$

WestCHEM, Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland, UK. E-mail: L.Cronin@chem.gla.ac.uk; Web: http://www.chem.gla.ac.uk/staff/lee; Fax: +44 (0)141-330-4888; Tel: +44 (0)141-330-6650
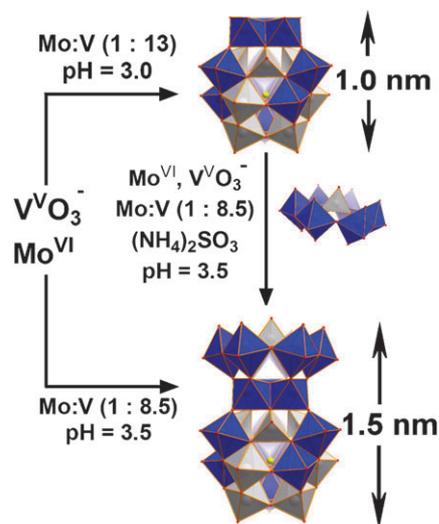
Fig. 1 Polyhedral presentation of {$Mo_{17}V_8$} **1a** (bottom) and the {$Mo_{11}V_7$} (top). The Mo centres are shown in blue, V in grey and the S of the sulfite anion is shown in yellow.

bridging anion, which occupies the central part of the lower hemisphere; that is the third reported example of the bridging mode found here.[4,8e] Whilst the Mo and V atoms are crystallographically distinguishable in the upper hemisphere and in the "crown" moiety, the metal sites in the bottom hemisphere are disordered. Therefore, the assignment of formal charges on the metal ions was made on the basis of charge balance considerations for the entire compound, combined with bond valence sum (BVS) calculations,[12] redox titrations,† and elemental analysis§ as well as high resolution cryospray mass spectrometry.† All the Mo atoms have the formal oxidation state VI (BVS$_{av}$ = 5.99), the V atoms in the VO_4 tetrahedra are in the oxidation state V (BVS = 5.05), whilst two out of the four V atoms in the bottom hemisphere are in the oxidation state IV (BVS M9, M20 = 4.25) and the remaining two are in the oxidation state V (BVS = 4.60). The V atoms in the VO_4 tetrahedra are coordinated by three μ_3-O^{2-} moieties, with V–O bonds spanning the range 1.728(6)–1.774(6) Å, and one terminal oxo group with V=O bonds of 1.627(9) and 1.634(7) Å respectively. The Mo atoms in the MoO_6 octahedra belonging to the upper hemisphere are coordinated by two terminal oxo groups in *cis*-positions, with Mo=O bonds spanning 1.686(7)–1.732(7) Å, one μ-O^{2-}, with Mo–O bonds spanning 1.882(8)–1.914(7) Å, and three μ_3-O^{2-} moieties, with Mo–O bonds spanning 1.935(8)–2.429(8) Å.

It is interesting to note the existence of the di–oxo Mo units on the cap of the distorted Dawson structure,[8e] which were considered inert due to the site on the cap being electronically saturated, and as a consequence non-reactive. In this case, and in contrast to this preliminary observation, we proved that this site of the molecule is possible to react efficiently in the presence of appropriate building units under controlled experimental conditions to give novel structural motifs, whilst at the same time retains the structural and chemical information from the parent molecule. Indeed, our structural analysis shows that compound **1** incorporates 6 dioxo-Mo units in the "crown" formation. This makes compound **1** an excellent candidate for use in the assembly of even larger nanoscale

clusters since it can potentially be used as a 'third generation' synthon, building on the previous assembly steps.

In an effort to extend our studies as well as to observe experimentally the "information" transferred from the parent molecule to the daughter product, we used the [$Mo^{VI}_{11}V^V_5V^{IV}_2O_{52}(\mu_9\text{-}SO_3)$]$^{7-}$ as a secondary building unit (SBU) in an effort to *directly* construct compound **1**, to see if the observed structural evolution process takes place. Addition of 0.15 g of $(NH_4)_6Mo_7O_{24}$ and 0.1 g NH_4VO_3 followed by adjustment of the pH at the value of 3.5 with small amounts of $(NH_4)_2SO_3$ in a stirred solution of {$Mo_{11}V_7$} led to the isolation of single crystals suitable for X-ray structural analysis of the $(NH_4)_{10}[Mo^{VI}_{11}V^V_5V^{IV}_2O_{52}(\mu_9\text{-}SO_3)(Mo^{VI}_6V^VO_{22})]\cdot14H_2O$ **1** in 52% yield (Fig. 1). The role of the sulfite anion for this transformation is very important, as has been proven in previously reported studies.[8,9] In this case the reduction of the V^V metal centres as well as the adjustment of the pH value offered by the sulfite anions triggers the aggregation and finally the structural evolution of the parent molecule towards the formation of compound **1** (Fig. 1).

During the course of this study, CSI-MS studies† have proven to be a powerful tool[5,13] in our effort to unveil the novel "Crowned" Dawson type cluster in solution, allowing **1a** to be identified prior to structural analysis, and to examine its structural evolution. In these studies, the Pr_4N salts of the {$Mo_{17}V_8$} cluster **1a**, dissolved in acetonitrile confirmed that the sulfite-capsule retains its integrity in solution, see Fig. 2, and peaks are seen which are assigned to {$(Pr_4N)_7[H_nV^V_{4-n}V^{IV}_{3+n}Mo_{11}O_{52}(SO_3)(Mo^{VI}_6V^VO_{22})](NH_4)_2(CH_3CN)$}$^{2-}$ where n = 0 (with three vanadium ions in oxidation state IV) giving an envelope centred at m/z *ca.* 2342.1, and where n = 1 (with four vanadium ions in oxidation state IV, requiring one proton) giving an envelope centred at m/z *ca.* 2342.6.

Importantly, the presence of ammonium cations proved to be crucial for the synthesis of the compound **1**, whereas using Na^+ or K^+ instead of NH_4^+ cations along with TEA yields
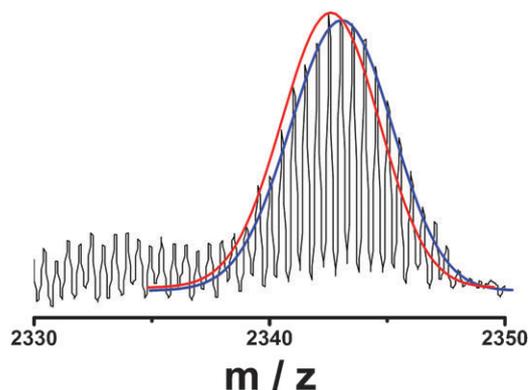
Fig. 2 Negative ion mass spectrum in acetonitrile solution of {$(Pr_4N)_7[H_nV^V_{4-n}V^{IV}_{3+n}Mo_{11}O_{52}(SO_3)(Mo^{VI}_6V^VO_{22})](NH_4)_2(CH_3CN)$}$^{2-}$. Two envelopes can be seen where n = 0 (with three vanadium ions in oxidation state IV) giving an envelope centred at m/z *ca.* 2342.1, and where n = 1 (with four vanadium ions in oxidation state IV, requiring one proton) giving an envelope centred at m/z *ca.* 2342.6. Black line: experimental data, red/blue lines: profile lines of the simulated isotope patterns.
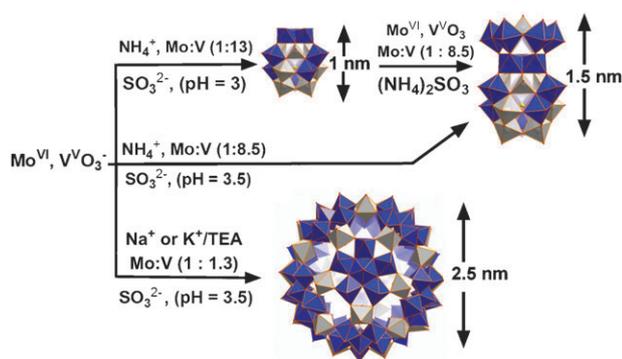
Fig. 3 Polyhedral presentation of {Mo$_{11}$V$_7$} (top-left), {Mo$_{17}$V$_8$} (top-right) and the {Mo$_{72}$V$_{30}$} (bottom). All the Mo centres are shown in blue while the V ones in grey. The scheme represents the conditions which lead to control of the assembly process and the structural transformations between the POM species. Mo: blue; V: grey.

the gigantic Keplerate architecture (a class of molecule first discovered by Müller)[14] with the formula {Mo$_{72}$V$_{30}$(SO$_4$)$_{12}$}[15] and dimensions of 2.5 nm (see ESI† for more information), see Fig. 3.

In conclusion, we have reported the synthesis and structural studies of an unprecedented mixed metal sulfite Dawson-based structure (NH$_4$)$_{10}$[Mo$^{VI}_{11}$V$^V_5$V$^{IV}_2$O$_{52}$(μ$_9$-SO$_3$) (Mo$^{VI}_6$V^{V}O$_{22}$)]·14H$_2$O **1**, and a ligand triggered structural evolution process of the parent cluster {Mo$_{11}$V$_7$} to {Mo$_{17}$V$_8$} which is the largest sulfite based POM reported so far. In addition we have shown that it is possible to utilize the reactive non-lacunary polyoxometalate-based species as synthons to trigger the formation of new cluster types, as well as demonstrating a parent-to-child 'crowning' of the precursor {Mo$_{11}$V$_7$}. In further studies, we will try and extend this building block approach as well as more detailed studies aimed at understanding the mechanistic details of the assembly of the {Mo$_{72}$V$_{30}$} Keplerate cluster.

Notes and references

‡ Crystal data for **1**: (NH$_4$)$_{10}$[Mo$^{VI}_{11}$V$^V_5$V$^{IV}_2$O$_{52}$(μ$_9$-SO$_3$)(Mo$^{VI}_6$V^{V}O$_{22}$)]·14H$_2$O: H$_{68}$Mo$_{17}$N$_{10}$O$_{91}$S$_1$V$_8$, M_r = 3735.20, orthorhombic, space group Pnma, a = 15.6986(5), b = 21.4976(3), c = 25.9861(3) Å, $\alpha = \beta = \gamma = $ 90°, V = 8769.85(3) Å^3, Z = 4, ρ_{calc} = 2.829 g cm^{-3}, T = 150(2) K, R_1(final) = 0.0544, wR_2 = 0.1518. Further details on the crystal structure investigation may be obtained from the Fachinformationenzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +49 7247-808-132, email: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-422196.

§ Ammonium molybdate tetrahydrate (0.60 g, 0.4 mmol) was dissolved in an HCl solution (37% HCl in water, 1 : 4 v/v, 25 mL, pH ≈ 0), and then solid ammonium metavanadate (0.40 g, 3.4 mmol) was added in one portion to the solution under stirring. Then, solid (NH$_4$)$_2$SO$_3$ (9.33 g, 69.5 mmol) was gradually added under stirring. Compound (**1**) could be synthesized within the pH range 2–4. The solution was filtered off and the filtrate left in an open vessel (a 100 mL beaker) at room temperature (∼25 °C) for a week, during which time dark green crystals suitable for X-ray structure analysis were obtained. During the crystallization time the dark green solution turns to deep purple. At this point the solution needs to be filtered off to avoid the

formation of by-products. The first yield of crystals appear while the solution is purple. The crystallization process continues till the point where the mother liquor has light green colour. Yield 0.11 g (56% based on Mo). Elemental analysis for: H$_{68}$Mo$_{17}$N$_{10}$O$_{91}$S$_1$V$_8$; calc: Mo: 43.67, V: 10.91%; found: Mo: 43.98, V: 10.95%. FT-IR [(KBr) v/cm^{-1}] 3442 (br) [ν(O–H) from H$_2$O], 1613 (s) [ν(NH$_4$)], 1401 [ν(SO$_3^{2-}$)], 962 (sh) [ν(V=O)], 944 [ν(Mo=O)], 895 (s) [ν(SO$_3^{2-}$)], 872 (s) [ν(SO$_3^{2-}$)], 812 (vs.) [ν(SO$_3^{2-}$)]. Vis (in H$_2$O): λ_{max}, [nm, (dm^3 mol^{-1} cm^{-1})] = 610.5(2400), 800(1868). −ve (negative) mode CSIMS at 20 °C in CH$_3$CN {(Pr$_4$N)$_7$[H$_n$V$^V_{4-n}$V$^{IV}_{3+n}$Mo$_{11}$O$_{52}$(SO$_3$)(Mo$^{VI}_6$V^{V}O$_{22}$)](NH$_4$)$_2$(CH$_3$C-N)}$^{2-}$ where n = 0 gives an envelope centred at m/z ca. 2342.1 and where n = 1 an envelope centred at m/z ca. 2342.6 as confirmed by isotopic fitting of the envelopes to the bifurcated isotopic distribution shown between 2336 and 2348 mass units.

1 (a) D.-L. Long, E. Burkholder and L. Cronin, Chem. Soc. Rev., 2007, **36**, 105; (b) D.-L. Long, R. Tsunashima and L. Cronin, Angew. Chem., Int. Ed., 2010, **49**, 1736.
2 (a) D.-L. Long, H. Abbas, P. Kögerler and L. Cronin, J. Am. Chem. Soc., 2004, **126**, 13880; (b) D.-L. Long, P. Kögerler, L. J. Farrugia and L. Cronin, Angew. Chem., Int. Ed., 2003, **42**, 4180; (c) D.-L. Long, P. Kögerler and L. Cronin, Angew. Chem., Int. Ed., 2004, **43**, 1817.
3 H. N. Miras, J. Yan, D.-L. Long and L. Cronin, Angew. Chem., Int. Ed., 2008, **47**, 8420.
4 H. N. Miras, G. J. T. Cooper, D.-L. Long, H. Bögge, A. Müller, C. Streb and L. Cronin, Science, 2010, **327**, 72.
5 H. N. Miras, E. F. Wilson and L. Cronin, Chem. Commun., 2009, 1297.
6 C. du Peloux, A. Dolbecq, P. Mialane, J. Marrot, E. Riviere and F. Secheresse, Angew. Chem., Int. Ed., 2001, **40**, 2455.
7 K. Y. Matsumoto, M. Kato and Y. Sasaki, Bull. Chem. Soc. Jpn., 1976, **49**, 106.
8 (a) M. J. Manos, H. N. Miras, V. Tangoulis, J. D. Woolins, A. M. Z. Slawin and T. A. Kabanos, Angew. Chem., Int. Ed., 2003, **42**, 425; (b) H. N. Miras, R. G. Raptis, P. Baran, N. Lalioti, M. P. Sigalas and T. A. Kabanos, Chem.–Eur. J., 2005, **11**, 2295; (c) D. L. Long, H. Abbas, P. Kögerler and L. Cronin, Angew. Chem., Int. Ed., 2005, **44**, 3415; (d) N. I. Kapakoglou, P. I. Betzios, S. E. Kazianis, C. E. Kosmidis, C. Drouza, M. J. Manos, M. P. Sigalas, A. D. Keramidas and T. A. Kabanos, Inorg. Chem., 2007, **46**, 6002; (e) H. N. Miras, D. J. Stone, E. J. L. McInnes, R. G. Raptis, P. Baran, G. I. Chilas, M. P. Sigalas, T. A. Kabanos and L. Cronin, Chem. Commun., 2008, 4703.
9 J. Yan, D.-L. Long, H. N. Miras and L. Cronin, Inorg. Chem., 2010, **49**, 1819.
10 (a) A. M. Todea, A. Merca, H. Bögge, T. Glaser, J. M. Pigga, M. L. K. Langston, T. Liu, R. Prozorov, M. Luban, C. Schroder, W. H. Casey and A. Müller, Angew. Chem., Int. Ed., 2010, **122**, 524; (b) D.-L. Long, Y.-F. Song, E. F. Wilson, P. Kögerler, S.-X. Guo, A. Bond, J. Hargreaves and L. Cronin, Angew. Chem., Int. Ed., 2008, **47**, 4384; (c) Q. Yin, J. M. Tan, C. Besson, Y. V. Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle and C. L. Hill, Science, 2010, **328**, 342.
11 A. Müller, E. Beckmann, H. Bögge, M. Schmidtmann and A. Dress, Angew. Chem., Int. Ed., 2002, **41**, 1162.
12 R. D. Shannon, Acta Crystallogr., Sect. A, 1976, **32**, 751.
13 (a) D. L. Long, P. Kögerler, A. D. C. Parenty, J. Fielden and L. Cronin, Angew. Chem., Int. Ed., 2006, **45**, 4798; (b) H. N. Miras, D.-L. Long, P. Kögerler and L. Cronin, Dalton Trans., 2008, 214.
14 A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann and F. Peters, Angew. Chem., Int. Ed., 1998, **37**, 3360.
15 (a) A. Müller, A. M. Todea, J. van Slageren, M. Dressel, H. Bögge, M. Schmidtmann, M. Luban, L. Engelhardt and M. Rusu, Angew. Chem., Int. Ed., 2005, **44**, 3857; (b) B. Botar, P. Kögerler and C. L. Hill, Chem. Commun., 2005, 3138.