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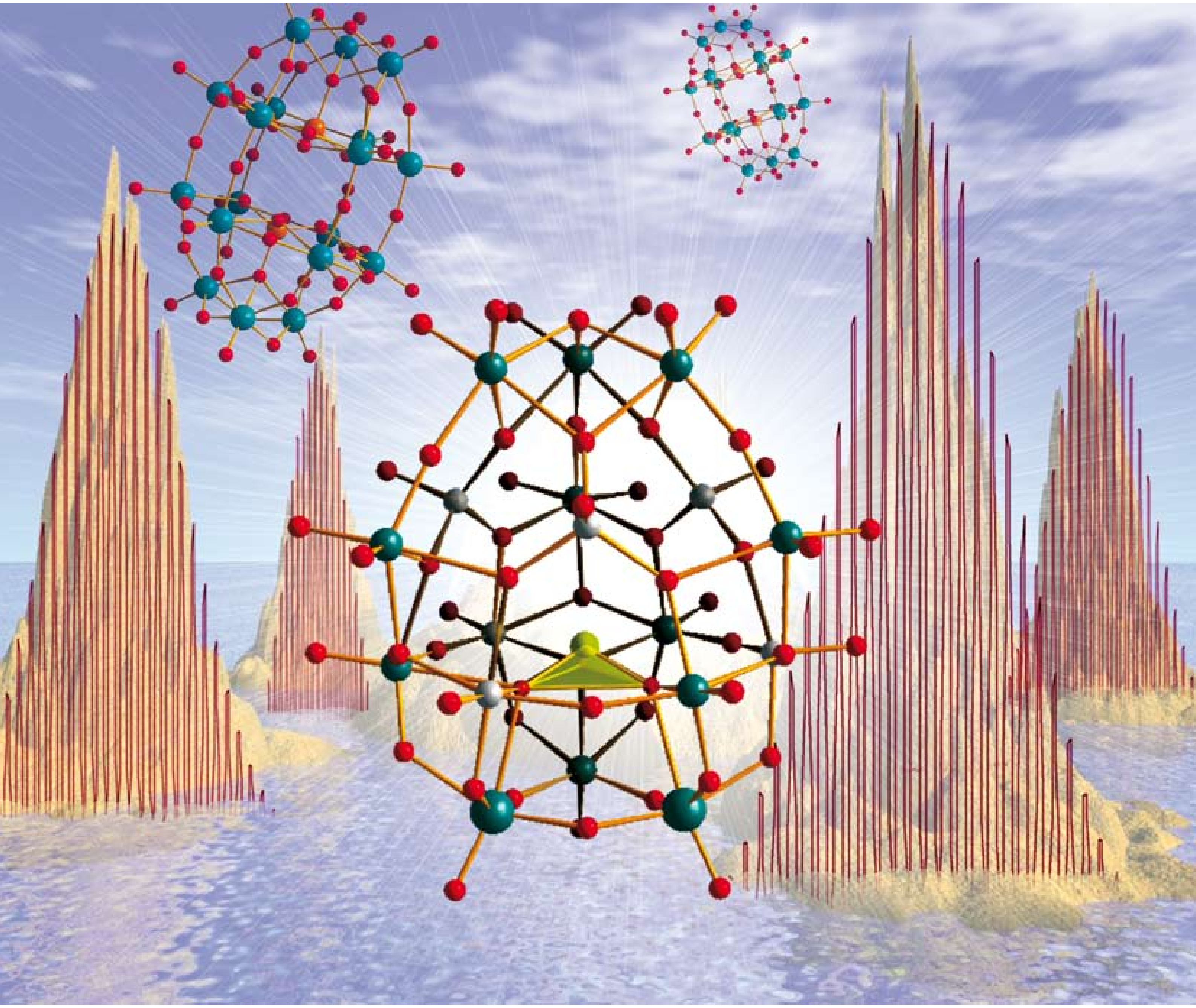

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FEATURE ARTICLE
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A polyoxomolybdenum/vanadium-sulfite $\{M_{18}\}$ cluster-based compound, $[Mo^{VI}_{11}V^{V}_{5}V^{IV}_{2}O_{52}(\mu_9\text{-}SO_3)]^{7-}$, is reported that exhibits a unique structural motif, arising from the incorporation of five V^{V} and two V^{IV} ions into a $\{M_{18}\}$ cluster framework templated by SO_3^{2-}; this cluster compostion was first identified using cryospray mass spectrometry.

The great interest in polyoxometalates (POMs) reflects the diverse nature of this family of inorganic clusters,[1] which exhibit a wide variety of compositions and structural versatility,[2] as well as important optical,[3] catalytic[4] and magnetic[5] properties. Most attention has been given to heteropolyanions containing tetrahedral phosphate groups because of their fascinating electronic and structural properties.[6] However, it is becoming clear that the incorpration of other heteroanions can have a profound effect on the functionality of the cluster. For example, the use of the sulfite anion[7] has allowed clusters with interesting physical properties (*e.g.* thermochromism and bistability) to be engineered.[8] This is because the C_{3v}-symmetric sulfite anion contains a non-bonding but stereochemically active lone pair of electrons, which can help impart additional redox and photophysical properties, meaning that studies involving the redox-active sulfite anion are important.[9]

An important subset of POMs are the Dawson species of the general formula $[M_{18}O_{54}(\mu_9\text{-}XO_4)_2]^{m-}$ (M = Mo, W; X = P^{V}, As^{V}, *etc.*), which comprise eighteen metal atoms in an oxo cage, containing heteroanions.[10] This is because they are highly derivatisable, whereby, until now, up to a maximum of three of the eighteen framework metals have been replaced by hetero-metals, such as Ti, Si, V, Nb, Ni, Co, Mn and Cu.[11] Here, we report a new structure type that is related in terms of cage geometry to the Dawson archetype, but where seven of the metal centres have been changed for hetero-metals, in this case $V^{V/IV}$ to give $(NH_4)_7[Mo^{VI}_{11}V^{V}_{5}V^{IV}_{2}O_{52}(\mu_9\text{-}SO_3)]\cdot 12H_2O$ (**1**), which we have identified using ESI mass spectrometry. Furthermore, this new structural archetype differs from normal Dawson-like structures since it only includes one templating heteroanion. The mixed valent nature of this compound is explored by structural methods and EPR spectroscopy, along with electrospray mass spectrometry, which was used to discover the new cluster type. This technique also demonstrates that the cluster is stable in solution.

In general, the discovery of new cluster systems, followed by systematic design, leading to functional nanoscale cluster systems, is a grand challenge in inorganic cluster chemistry. This is because true design approaches lead to a new type of molecular nanotechnology that involves functional nanoscale clusters built using self-assembly from the 'bottom-up'.[12] In this respect, we have utilised mass spectrometry to 'scan' the reaction systems to help identify potentially new and interesting cluster architectures. The sequential addition of solid $NH_4V^{V}O_3$ and $(NH_4)_2SO_3$ in an acidified aqueous (37% HCl in water, 1 : 4 v/v) solution of $(NH_4)_6Mo_7^{VI}O_{24}$ resulted in the formation of the deep green material of compound **1**.‡ The initial investigation of this material using mass

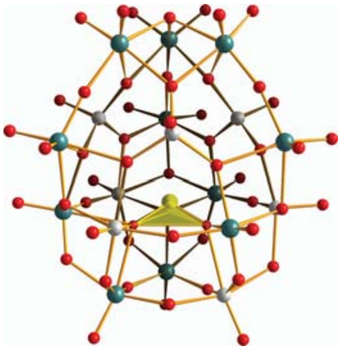

Fig. 1 A ball-and-stick representation of the anion of **1**. Average bond lengths (Å): Mo═O 1.685(4), Mo–O(μ-O) 1.879(5), Mo–O(μ₃-O) 2.095(3), Mo–O(μ-O–SO₂) 2.394(17), V═O 1.610(5), V–O(μ-O) 1.892(6), V–O(μ₃-O) 1.901(25) and V–O(μ-O–SO₂) 2.477(28). Colour scheme: Mo—green, O—red, V—grey, S—yellow polyhedra.

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† Electronic supplementary information (ESI) available: Details and graphs describing the REDOX titrations, CSI-MS and K-band (10 K), and X-band (300 K) EPR spectra for compound **1**. CCDC 693611. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b811279g

spectrometry (*via* ion exchange with organic cations) allowed **1a** to be roughly identified as a mixed Mo/V cluster in the ratio $Mo_{11}V_7$; the subsequent crystallisation of **1** allowing solid state characterisation. At this point, it is worth noting two interesting features: (a) the existence of the oxidized form of V in the presence of a reducing agent, even though the V^V is reduced rapidly to V^{IV} by sulfite[8b,c] (in the present case there are five V^V); (b) a plethora of geometries are adopted by the metal centres in the same structure, as shown by structural analysis. The X-ray structure analysis§ revealed that compound **1** consists of the anion $[Mo^{VI}_{11}V^{V}_{5}V^{IV}_{2}O_{52}(\mu_9\text{-}SO_3)]^{7-}$ (**1a**), shown in Fig. 1, as well as seven NH_4^+ counterions.

The anion $[Mo^{VI}_{11}V^{V}_{5}V^{IV}_{2}(O)_{52}(\mu_9\text{-}SO_3)]^{7-}$ adopts a Dawson-like structure. The distorted egg-shaped capsule of the molybdovanadate-sulfite anion is built up from two different hemispheres. In the upper hemisphere, three edge-sharing MoO_6 octahedra form the cap, which is connected to the belt *via* vertexes of alternating V^VO_4 tetrahedra and MoO_6 octahedra; both the Mo and V positions are well defined with no disorder. However, the remaining four V positions (two V^V and two V^{IV}; see below for details) are crystallographically refined as being disordered in the bottom part of the cluster over nine potential positions. This means that the $\{M_6\}$ belt in the bottom hemisphere is made of three sets of edge-sharing MoO_6/VO_6 octahedra interconnected within the framework to give three Mo–O–V moieties arranged in the ring on average. Finally, the $\{M_3\}$ cap of the bottom of the cluster (below the SO_3^{2-} group in Fig. 1) contains two Mo and one V position, respectively. One important structural aspect is the presence of the μ_9-SO_3 bridging anion, which occupies the central part of the lower hemisphere; each of the three oxygen atoms of the pyramidal SO_3^{2-} moiety ligates the Mo/V atoms, one from the cap and two from the belt, in a bridging mode. In a classical Dawson cluster, one of the four oxygen atoms of the tetrahedral XO_4 moiety is ligated to the three capping metal centers, while the remaining three oxygen atoms each bridge two of the six metal atoms of the belt of the same hemisphere. Whilst the Mo and V atoms are clearly distinguishable in the upper hemisphere crystallographically, the metal sites in the bottom hemisphere are disordered. Therefore, the assignment of formal charges on the metals was made on the basis of charge balance considerations for the entire compound, combined with BVS calculations,[13] redox titrations,† elemental analysis‡ and EPR, as well as high resolution cryospray and electrospray mass spectrometry.† All the Mo atoms have the formal oxidation state VI (BVS = 6.07), the V atoms in the VO_4 tetrahedra are in the oxidation state V (BVS = 5.1), whilst two out of the four V atoms in the bottom hemisphere are in the oxidation state IV (BVS M7, M7′ = 4.2) and the remaining two are in the oxidation state V (BVS = 4.73). The V atoms in the VO_4 tetrahedra are coordinated by three μ_3-O^{2-} moieties, with V–O bonds spanning the range 1.723(3)–1.763(3) Å, and one terminal oxo group with V═O bonds of 1.636(4) or 1.642(5) Å. 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 1.698(3)–1.714(4) Å, one μ-O^{2-}, with Mo–O bonds spanning 1.867(4)–1.892(4) Å, and three μ_3-O^{2-} moieties, with Mo–O bonds spanning 2.018(4)–2.271(3) Å. An important structural difference between the M_{18} cluster presented here and its classical parent Dawson structures, ($[M_{18}O_{54}(\mu_9\text{-}XO_4)_2]^{n-}$ and $[M_{18}O_{54}(\mu_9\text{-}SO_3)_2]^{n-}$ [8d,e]), is the presence of three tetrahedral V^V atoms in the belt of the upper hemisphere, instead of the three MO_6 octahedra in the Dawson species. These three tetrahedral V^V atoms prevent the incorporation of a second SO_3^{2-} into the upper hemisphere due to steric limitations. Furthermore, the V centers in **1a** are located only 4.751(2) Å away from each other, while in the classic Mo Dawson structure, the equivalent Mo centers lie 6.134(1) Å apart. As a consequence, there is a larger internal volume in the classical Dawson structure that allows the incorporation of the two tetrahedral heteroanions. As such, the presence of the three V tetrahedra in **1a** modifies the connectivity of the MO_6 octahedra in relation to their corresponding classical Dawson clusters, where there are six groups of three edge-sharing octahedra (Fig. 2) and the Mo_3V_3 metal atoms of the belt of the upper hemisphere are not co-planar (see Fig. 2).

Fig. 2 A polyhedral representation of the anion for compound **1** (right) and for the classical Dawson $[Mo_{18}O_{54}(\mu_9\text{-}XO_4)_2]^{n-}$ moiety (left). Colour scheme: Mo—red/blue polyhedra, P—orange polyhedra, V—grey polyhedra, S—yellow sphere.

Finally, each of the six Mo^{VI} atoms of the upper hemisphere of **1a** support two terminal oxo groups, which is in marked contrast to the metal atoms (Mo, W) in the $[M_{18}O_{54}(\mu_9\text{-}XO_4)_2]^{n-}$ and $[M_{18}O_{54}(\mu_9\text{-}SO_3)_2]^{n-}$ clusters,[8d,e] each of which only support one terminal oxo group. The presence of V^{IV} was confirmed by EPR, with a characteristic hyperfine coupling to ^{51}V in the solid state ($I = 7/2$, 100%; Fig. 3, ESI Fig. S2†). Low temperature spectra could be simulated as a single V^{IV} centre, giving $g_x = 1.981$, $g_y = 1.965$, $g_z = 1.946$, $A_x = A_y = 45$ and $A_z = 137 \times 10^{-4}\ cm^{-1}$.[14] The rhombic parameters are consistent with the site symmetries of the metal ions. However, the A_z hyperfine component is unusually small for a oxidovanadium(IV) species (typically $180 \times 10^{-4}\ cm^{-1}$). Such small couplings have been observed for non-

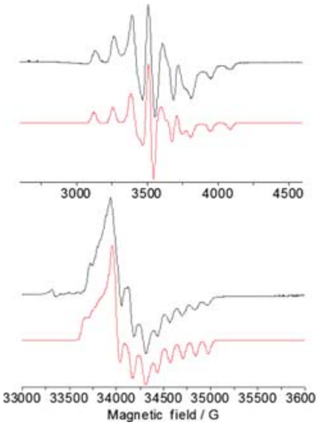

Fig. 3 Solid state X- (top) and W-band (bottom) EPR spectra of **1** at 10 K (black) and simulations (red).

oxo V^{IV}, but this is not consistent with the X-ray structure of **1**. The only other explanation is a substantial delocalisation of the unpaired electron from the vanadyl ion. Reduced A_z values ($\approx 150 \times 10^{-4}$ cm^{-1}) have also been observed in the $[W_{15}V^{IV}V^{V}{}_2O_{54}(PO_4)_2]^{10-}$ Dawson ion.[15] In the latter compound, the V ions form one of the M_3 caps, and delocalisation is confirmed by the observation of a weak coupling to a second ^{51}V nucleus. We do not observe secondary coupling in **1a**, which may indicate that the V ions are not adjacent; this is also consistent with the lack of any features characteristic of magnetic exchange interactions. Finally, the temperature dependence of the linewidths, changing from *ca.* 70 to 20 G upon cooling from 300 to 100 K but not changing below this (ESI Fig. S3†), is characteristic of the onset of electron hopping effects between V^{IV} and V^{V} at higher temperatures.

During the course of this study, CSI-MS† proved to be a powerful tool[16] in our efforts to unveil new Dawson-like clusters in solution, allowing **1a** to be identified in solution prior to structural analysis. CSI-MS studies of the Pr_4N salts of cluster **1a** dissolved in acetonitrile confirmed that the sulfite capsule retained its integrity in solution (ESI Fig. S4†), and peaks were seen that were assigned to $\{(Pr_4N)_4[H_{1-n}V^{V}{}_{5+n}V^{IV}{}_{2-n}Mo_{11}O_{52}(SO_3)]\}^{2-}$ where $n = 1$ (with only one vanadium ion in oxidation state IV), giving an envelope centred at *m*/*z ca.* 1534.5, and where $n = 0$ (with two vanadium ions in oxidation state IV, requiring one proton), giving an envelope centred at *m*/*z ca.* 1535.0.

In conclusion, a mixed metal polyoxomolybdenum/vanadium-sulfite cluster compound has been presented that was identified *in solution* using mass spectrometry. After the compound was identified, it was produced in a pure phase and characterised crystallographically, by EPR, chemical analysis, BVS and redox titrations. Importantly, the observation of the *in situ*-formation and stability of modified Mo/V Dawson capsules using mass spectrometry proved to be crucial in terms of observing the self-assembly of new POM clusters with novel structural features, *e.g.* establishing the existence of the sulfite-based pyramidal template within the cluster shell, as well as the mixed metal Mo/V cluster. The combination of Mo and V with the pyramidal sulfite ligand resulted in the modification of the "M_{18}" oxide microstructure of **1a** to yield a unique structural motif. Thus, the template effect of the sulfite anion into the mixed metal Mo/V system could trigger the self-assembly of frameworks with novel structural features and potentially intriguing properties.[8d,e] In future work, we will systematically explore the $\{M_{18}\}$ parameter space to produce a range of heterometallic systems from $\{M_{15}V_3\}$ to $\{M_{11}V_7\}$, and also try to utilise the additional oxo groups that can be engineered into these systems in oxo transfer processes.

Notes and references

‡ $(NH_4)_6Mo_7{}^{VI}O_{24}\cdot 4H_2O$ (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 NH_4VO_3 (0.60 g, 5.1 mmol) was added in one portion to the solution under stirring. Upon dissolution of the NH_4VO_3, the light red colour of the solution changed to light green and the pH changed to 0.7. Then, solid $(NH_4)_2SO_3$ (6.20 g, 46.2 mmol) was gradually added under magnetic stirring. A series of colour changes ensued, beginning from a green colour at pH 0.7, then a light blue colour at pH 1.5, followed by the formation of a deep violet solution at pH 3. Compound **1** could be synthesized within the pH range 2.5–5, although the highest yield was obtained at pH 3. The solution was filtered off and the filtrate left in an open vessel (a 250 ml beaker) at room temperature (~25 °C) for 3 d, during which time deep green crystals suitable for X-ray structure analysis were obtained. Yield: 0.95 g (21% based on Mo).

§ Crystal data for **1**: $(NH_4)_7[Mo^{VI}{}_{11}V^{V}{}_5V^{IV}{}_2O_{52}(SO_3)]\cdot 12H_2O$: $H_{52}Mo_{11}N_7O_{67}SV_7$, $M_r = 2666.47$, monoclinic, space group $P2_1/m$, $a = 12.140(2)$, $b = 19.148(2)$, $c = 13.492(2)$ Å, $\beta = 105.653(2)°$, $V = 3020.1(1)$ Å^3, $Z = 2$, $\rho_{calc} = 2.898$ g cm^{-3}, $T = 150(2)$ K. Of 21908 measured reflections, 5765 were independent ($R_{int} = 0.0216$) and 5218 observed ($I > 2\sigma(I)$). $R1$ (final) = 0.0301, w$R2$ = 0.0846.†

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