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Solution identification and solid state characterisation of a heterometallic polyoxometalate \{Mo\textsubscript{11}V\textsubscript{7}\}: [Mo\textsuperscript{VI}\textsubscript{11}V\textsuperscript{V}\textsubscript{5}O\textsubscript{52}(\mu\textsubscript{9}-SO\textsubscript{3})]\textsuperscript{7−}†

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A polyoxomolybdenum/vanadium-sulfite \{M\textsubscript{18}\} cluster-based compound, [Mo\textsuperscript{VI}\textsubscript{11}V\textsuperscript{V}\textsubscript{5}O\textsubscript{52}(\mu\textsubscript{9}-SO\textsubscript{3})]\textsuperscript{7−}, is reported that exhibits a unique structural motif, arising from the incorporation of five V\textsuperscript{V} and two V\textsuperscript{IV} ions into a \{M\textsubscript{18}\} cluster framework templated by SO\textsubscript{3}\textsuperscript{2−}; this cluster composition was first identified using cryospray mass spectrometry.

The great interest in polyoxometalates (POMs) reflects the diverse nature of this family of inorganic clusters, which exhibit a wide variety of compositions and structural versatility, as well as important optical, catalytic and magnetic properties. Most attention has been given to heteropolyanions containing tetrahedral phosphate groups because of their fascinating electronic and structural properties. However, it is becoming clear that the incorporation of other heteroanions can have a profound effect on the functionality of the cluster. For example, the use of the sulfite anion has allowed clusters with interesting physical and photophysical properties, meaning that studies involving the redox-active sulfite anion are important.

An important subset of POMs are the Dawson species of the general formula \([\text{M}\textsubscript{12}O\textsubscript{42}(\text{XO}\textsubscript{4})\textsubscript{2}]^\textsuperscript{3−}\) (M = Mo, W; X = P, V, As, etc.), which comprise eighteen metal atoms in an oxo cage, containing heteroanions. 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they are highly derivatisable, whereby, until now, up to a maximum of three of the eighteen framework metals have been replaced by hetero-metals, such as Ti, Si, V, Nb, Ni, Co, Mn and Cu. 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\textsuperscript{V/IV} to give (NH\textsubscript{4})\textsubscript{7}[Mo\textsuperscript{VI}\textsubscript{11}V\textsuperscript{V}\textsubscript{5}O\textsubscript{52}(\mu\textsubscript{9}-SO\textsubscript{3})]\textsubscript{12}H\textsubscript{2}O (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’. 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\textsubscript{4}H\textsubscript{2}O\textsubscript{3} and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{3} in an acidified aqueous (37% HCl in water, 1 : 4 v/v) solution of (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24} resulted in the formation of the deep green material of compound 1.† The initial investigation of this material using mass
reduced rapidly to \( \text{V}^{IV} \) by sulfite, alternating \( \text{V}^{V} \) and \( \text{Mo}^{VI} \) via in the presence of a reducing agent, even though the \( \text{V}^{V} \) is interesting features: (a) the existence of the oxidized form of \( \text{V} \) is reduced rapidly to \( \text{V}^{IV} \) by sulfite, (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 \( \text{I} \) consists of the anion \([\text{Mo}^{VI}_{11}\text{V}^{IV}_{3}\text{V}^{IV}_{2}\text{O}_{2}\text{S}_{2}(\mu_3-\text{SO}_{3})]^{7-}\) (1a), shown in Fig. 1, as well as seven \( \text{NH}_{2}^{+} \) counterions.

The anion \([\text{Mo}^{VI}_{11}\text{V}^{IV}_{3}\text{V}^{IV}_{2}\text{O}_{2}\text{S}_{2}(\mu_3-\text{SO}_{3})]^{7-}\) 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 \( \text{MoO}_{6} \) octahedra form the cap, which is connected to the belt via vertexes of alternating \( \text{V}^{IV} \) tetrahedra and \( \text{MoO}_{6} \) octahedra; both the \( \text{Mo} \) and \( \text{V} \) positions are well defined with no disorder. However, the remaining four \( \text{V} \) positions (two \( \text{V}^{IV} \) and two \( \text{V}^{V} \); 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 \( \{\text{M}_{6}\} \) belt in the bottom hemisphere is made of three sets of edge-sharing \( \text{MoO}_{6}/\text{VO}_{4} \) octahedra interconnected within the framework to give three \( \text{Mo}--\text{O}--\text{V} \) moieties arranged in the ring on average. Finally, the \( \{\text{M}_{4}\} \) cap of the bottom of the cluster (below the \( \text{SO}_{3}^{2-} \) group in Fig. 1) contains two \( \text{Mo} \) and one \( \text{V} \) position, respectively. One important structural aspect is the presence of the \( \mu_3-\text{SO}_{3} \) bridging anion, which occupies the central part of the lower hemisphere; each of the three oxygen atoms of the pyramidal \( \text{SO}_{3}^{2-} \) moiety ligates the \( \text{Mo}/\text{V} \) 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 \( \text{XO}_{4} \) 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 \( \text{Mo} \) and \( \text{V} \) 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, redox titrations, elemental analysis and EPR, as well as high resolution cryospray and electrospray mass spectrometry. All the \( \text{Mo} \) atoms have the formal oxidation state \( \text{VI} \) (BVS = 6.07), the \( \text{V} \) atoms in the \( \text{VO}_{4} \) tetrahedra are in the oxidation state \( \text{V} \) (BVS = 5.1), whilst two out of the \( \text{V} \) atoms in the bottom hemisphere are in the oxidation state \( \text{IV} \) (BVS M7, M7' = 4.2) and the remaining two are in the oxidation state \( \text{V} \) (BVS = 4.73). The \( \text{V} \) atoms in the \( \text{VO}_{4} \) tetrahedra are coordinated by three \( \mu_3-\text{O}^{2-} \) moieties, with \( \text{V}--\text{O} \) bonds spanning the range 1.723(3)–1.763(3) Å, and one terminal oxo group with \( \text{V}--\text{O} \) bonds of 1.636(4) or 1.642(5) Å. The \( \text{Mo} \) atoms in the \( \text{MoO}_{6} \) octahedra belonging to the upper hemisphere are coordinated by two terminal oxo groups in cis-positions, with \( \text{Mo}--\text{O} \) bonds spanning 1.698(3)–1.714(4) Å, one \( \mu_3-\text{O}^{2-} \), with \( \text{Mo}--\text{O} \) bonds spanning 1.867(4)–1.892(4) Å, and three \( \mu_3-\text{O}^{2-} \) moieties, with \( \text{Mo}--\text{O} \) bonds spanning 2.018(4)–2.271(3) Å. An important structural difference between the \( \text{M}_{18} \) cluster presented here and its classical parent Dawson structures, \([\text{M}_{18}\text{O}_{54}(\mu_3-\text{XO}_{4})]^{8-}\) and \([\text{M}_{18}\text{O}_{54}(\mu_3-\text{SO}_{3})]^{8-}\), is the presence of three tetrahedral \( \text{V}^{V} \) atoms in the belt of the upper hemisphere, instead of the three \( \text{MoO}_{6} \) octahedra in the Dawson species. These three tetrahedral \( \text{V}^{V} \) atoms prevent the incorporation of a second \( \text{SO}_{3}^{2-} \) into the upper hemisphere due to steric limitations. Furthermore, the \( \text{V} \) centers in \( \text{I} \) are located only 4.751(2) Å away from each other, while in the classic Mo Dawson structure, the equivalent \( \text{Mo} \) 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 \( \text{V} \) tetrahedra in \( \text{I} \) modifies the connectivity of the \( \text{MoO}_{6} \) octahedra in relation to their corresponding classical Dawson clusters, where there are six groups of three edge-sharing octahedra (Fig. 2) and the \( \text{Mo}/\text{V} \) metal atoms of the belt of the upper hemisphere are not co-planar (see Fig. 2).

Finally, each of the six \( \text{Mo}^{VI} \) atoms of the upper hemisphere of \( \text{I} \) support two terminal oxo groups, which is in marked contrast to the metal atoms (\( \text{Mo} \), \( \text{W} \)) in the \([\text{M}_{18}\text{O}_{54}(\mu_3-\text{XO}_{4})]^{8-}\) and \([\text{M}_{18}\text{O}_{54}(\mu_3-\text{SO}_{3})]^{8-}\) clusters, each of which only support one terminal oxo group. The presence of \( \text{V}^{IV} \) was confirmed by EPR, with a characteristic hyperfine coupling to \( ^{51}\text{V} \) in the solid state \((I = 7/2, 100\%\); Fig. 3, ESI Fig. S2†). Low temperature spectra could be simulated as a single \( \text{V}^{IV} \) centre, giving \( g_x = 1.981 \), \( g_y = 1.965 \), \( g_z = 1.946 \), \( A_x = A_y = 45 \) and \( A_z = 137 \times 10^{-4} \text{ cm}^{-1} \). The rhombic parameters are consistent with the site symmetries of the metal ions. However, the \( A_z \) hyperfine component is unusually small for a oxidovanadanium(iv) species (typically \( 180 \times 10^{-4} \text{ cm}^{-1} \)). Such small couplings have been observed for non-

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**Fig. 2** A polyhedral representation of the anion for compound \( \text{I} \) (right) and for the classical Dawson \([\text{Mo}_{18}\text{O}_{54}(\mu_3-\text{XO}_{4})]^{8-}\) moiety (left). Colour scheme: Mo—red/blue polyhedra, P—orange polyhedra, V—grey polyhedra, S—yellow sphere.

**Fig. 3** Solid state X- (top) and W-band (bottom) EPR spectra of \( \text{I} \) at 10 K (black) and simulations (red).
oxo V\textsuperscript{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 \( A_2 \) values (\( \approx 150 \times 10^{-4} \text{ cm}^{-1} \)) have also been observed in the \([\text{W}_{15}\text{V}_5\text{O}_5\text{O}_2\text{S}(\text{PO}_4)]^{10-}\) Dawson ion.\textsuperscript{15} In the latter compound, the V ions form one of the \( M_1 \) caps, and delocalisation is confirmed by the observation of a weak coupling to a second \( ^5\text{V} \) 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\textsuperscript{a}), is characteristic of the onset of electron hopping effects between \( ^{15}\text{V} \) and \( ^{10}\text{V} \) at higher temperatures.

During the course of this study, CSI-MS\textsuperscript{f} proved to be a powerful tool\textsuperscript{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 \( \text{Pr}_2\text{N} \) salts of cluster 1a dissolved in acetonitrile confirmed that the sulfite capsule retained its integrity in solution (ESI Fig. S4\textsuperscript{a}), and peaks were seen that were assigned to \([\{\text{Pr}_2\text{N}\}H\cdots\text{V}^\text{II}\cdots\text{V}^\text{II}\cdots\text{V}^\text{II}\cdots\text{Mo}_{10}\text{O}_{50}(\text{SO}_3)]\)\textsuperscript{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 a conclusion, a mixed metal polyoxomolybdenum/vanadium-sulfite cluster compound has been presented that was identified in solution using mass spectrometry. After the compound was produced in a pure phase and characterised, it was synthesized within the pH range 2.5–5, although the highest yield was observed at pH 3. The solution was filtered off and the filtrate left in an open vessel (250 ml beaker) at room temperature (\( \approx 25 \text{ °C} \)) for 3 d, during which time deep green crystals suitable for X-ray structure analysis were obtained. Yield, 1.895 g (21% based on Mo).

Notes and references

14. Modelling multiple frequency EPR spectra (X,K,W-band) with consistent parameters is only possible by including an angle between the principal axes of the g and A matrices (\( 14^\circ \) about \( g_{\perp} \)). A detailed analysis of this low-symmetry phenomenon requires single crystal studies, which will be reported later.