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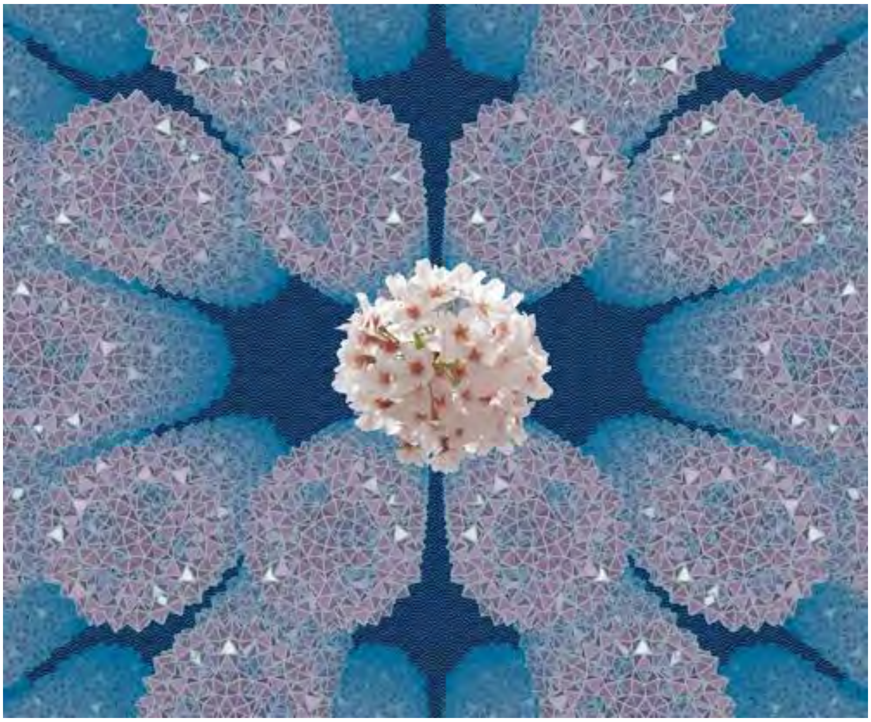

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COMMUNICATION

Cation induced structural transformation and mass spectrometric observation of the missing dodecavanadomanganate(IV)†

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The heteropolyvanadate cluster $[(n\text{-}C_4H_9)_4N]_4[Mn^{IV}V_{12}O_{34}]\cdot 2CH_3CN$ has been isolated by cation exchange from $K_{10}[(Mn^{IV}V_{11}O_{32})_2]\cdot 20H_2O$. The structural transformation has been confirmed by X-ray single crystal structure determination and cryospray ionization mass spectrometry measurements.

Polyoxometalates (POMs), as a unique class of anionic early transition-metal oxide clusters, have been receiving increasing attention not only for their unmatched structural diversity[1,2] but also for their potential applications in diverse disciplines including biology,[2–7] catalysis[8] and, in particular, the field of materials science.[9] Among the variety of different structures, the trinuclear unit $\{M_3O_{13}\}$, which is constructed from the condensation of three $\{MO_6\}$ octahedra, is by far the most common basic subunit in polyoxometalate chemistry. Heteropolyoxometalates (HPOMs) are usually highly symmetrical clusters assembled *via* the aggregation of $\{M_3O_{13}\}$ units centered around a templating heteroatom, in which the most common structures are Keggin and Wells–Dawson anions with tetrahedral $\{MO_4\}$ templates, and Anderson anions with octahedral $\{MO_6\}$ templates.[10] Recently, novel Dawson-like HPOM clusters have been discovered with octahedral (TeO_6, IO_6, WO_6)[11] and pyramidal (SO_3, TeO_3)[12,13] templates encapsulated within the $\{W_{18}\}$ shell. Compared to the extensive investigation of heteropolymolybdates and heteropolytungstates, the study of heteropolyvanadates is considerably less well developed. It is expected that the structure of such heteropolyvanadates should differ significantly from their molybdate and tungstate based counterparts due to the difference in oxidation state and relative structural flexibility of the vanadium(V) ion compared with molybdenum(VI) and tungsten(VI). This is therefore a major factor motivating the exploration of new types of heteropolyvanadate clusters.

Decades ago, Pope *et al.* conducted a detailed investigation of heterpolyvanadomanganate species in aqueous solution. That work found two main species; an undecavanadomanganate-based dimer, $K_{10}[(Mn^{IV}V_{11}O_{32})_2]\cdot 20H_2O$, in which the $\{MnV_{11}\}_2$ cluster units possess C_{2h} symmetry,[14,15] and triskaidecavanadomanganate $K_7[Mn^{IV}V_{13}O_{38}]\cdot 18H_2O$, wherein the $\{MnV_{13}\}$ unit exists with C_{2v} symmetry,[16] together with one by-product, $K_5H_3[Mn_3^{IV}V_{12}O_{40}]\cdot 8H_2O$,[14,15] which has an overall C_{3v} symmetry. The stoichiometry of Mn : V in these compounds is 1 : 11, 1 : 13 and 1 : 4 (3 : 12), respectively, which provoked us to question why no 1 : 12 species had thus far been observed. From Pope's results, it was reported that they could not obtain new species either through modification of the Mn : V ratio, or by variation of the reaction pH. It is, however, well accepted in polyoxometalate chemistry that both the size and type of the cation can play a crucial role in determining the assembly processes of the products formed.[17] Herein, we report the use of a cation exchange reaction – substituting the classical inorganic cation K^+ for the quaternary *n*-tetrabutylammonium (TBA) organic cation – in order to successfully isolate the hypothetical 12-vanadomanganate species $[(n\text{-}C_4H_9)_4N]_4[Mn^{IV}V_{12}O_{34}]\cdot 2CH_3CN$ (**1**).‡

Compound **1** was synthesized by reacting $K_{10}[(Mn^{IV}V_{11}O_{32})_2]\cdot 20H_2O$ with tetrabutylammonium bromide (TBABr) in aqueous solution. Single crystals were obtained by diffusion of diethyl ether into an acetonitrile solution of **1**. The single-crystal X-ray analysis revealed that compound **1** is a highly condensed heteropolyoxovanadate cluster showing a layered structural motif with C_{3v} symmetry (as shown in Fig. 1). The polyoxoanion consists of twelve edge-shared $\{VO_6\}$ octahedra with a $\{MnO_6\}$ unit located in the center. The cluster $[Mn^{IV}V_{12}O_{34}]$ can be divided into two layers: $\{MnV_6\}$ and $\{V_6\}$, whereby the $\{MnV_6\}$ layer is analogous to the Anderson type anion in that the Mn atom is surrounded by a ring of six V atoms and bonded to three μ_3-O and three μ_6-O atoms. The Mn–O bond length ranges are 1.865(5)–1.936(5) Å and O–Mn–O angles are 85.0(2)–172.7(2)°. The $\{V_6\}$ layer is composed of three V atoms forming a triangular unit, which is flanked by another three V atoms on the three sides of the triangle. The two layers then share the central twelve oxygen atoms to form the condensed $\{MnV_{12}\}$ cluster. The V–O bond lengths are in the range 1.572(6)–2.406(5) Å and O–V–O angles

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† Electronic supplementary information (ESI) available: Synthesis, experimental details, mass spectrometry, cyclic voltammetry, TGA/DSC and IR studies. CCDC 872161. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30627a

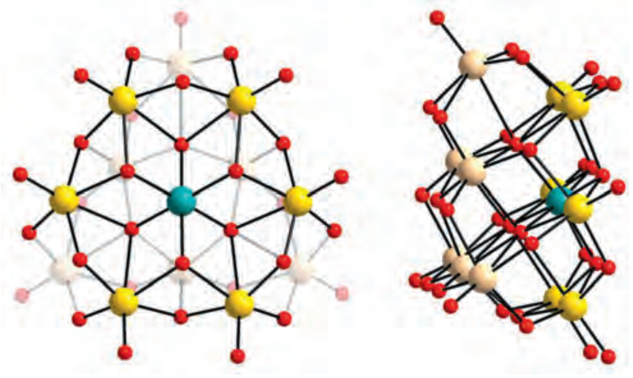

Fig. 1 Ball and stick representation of the $[MnV_{12}O_{34}]^{4-}$ cluster in **1**. Left: top down view highlighting the Anderson-type-like structure of the MnV_6 layer, right: side-on view. Colour code: V in MnV_6 layer = yellow, V in V_6 layer = tan, Mn = teal, O = red.

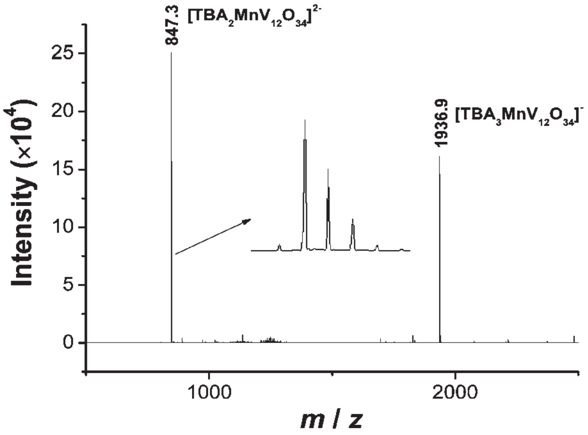

Fig. 2 The negative ion mass spectrum of the TBA^+ salt of **1** in acetonitrile showing different charged forms of $\{MnV_{12}O_{34}\}$. The inset shows the expansion of the peak at m/z = 847.3.

are in the range of 73.09(19)–175.9(2)°. Bond valence sums (BVS)[18,19] showed that all V atoms are in +5 oxidation state, the Mn atom in a +4 oxidation state and all O atoms in a −2 state.

High-resolution electrospray and cryospray mass spectrometry (MS)[20] was performed to determine the exact components of the dodecavanadomanganate cluster. Fig. 2 shows the negative ion mode mass spectra of **1** in acetonitrile in which both the major peaks can be assigned to anion fragments related to $\{MnV_{12}\}$. The peak centered at m/z = 1936.9 corresponds to $[(TBA)_3Mn^{IV}V_{12}O_{34}]^-$, and the peak centered at m/z = 847.3 can be assigned to $[(TBA)_2Mn^{IV}V_{12}O_{34}]^{2-}$. These results are in accordance with the single crystal X-ray analysis.

In subsequent experiments we also attempted to utilize TPA^+ (TPA = tetrapropylammonium) to replace K^+ and in this case, $(TPA)_4[Mn^{IV}V_{12}O_{34}]$ could also be isolated as a pure phase as confirmed by mass spectrometry (Fig. S1, see ESI†). The peak centered at m/z = 1768.7 corresponds to $[(TPA)_3Mn^{IV}V_{12}O_{34}]^-$, and the peaks centered at m/z = 1687.1 and 1605.5 are attributed to $[(TPA)_5Na(Mn^{IV}V_{12}O_{34})_2]^{2-}$ and $[(TPA)_4Na_2(Mn^{IV}V_{12}O_{34})_2]^{2-}$ (Na^+ from glass containers). Similarly, we also attempted to use the $K_7[Mn^{IV}V_{13}O_{38}]\cdot 18H_2O$ species in a cation exchange reaction with TBABr, and subsequently observed the formation of $(TBA)_4[Mn^{IV}V_{12}O_{34}]$ together with small amount of $[V_{10}O_{28}]^{6-}$ impurity. The mass spectrum is presented in Fig. 3, in which the strongest peak centered at m/z = 1937.0 corresponds to $[(TBA)_3Mn^{IV}V_{12}O_{34}]^-$, whilst decavanadate fragments $[(TBA)_2H_3V_{10}O_{28}]^-$ and $[(TBA)_2HV_{10}O_{27}]^-$ can be observed at m/z = 1444.9 and 1426.9. The species of $[(TBA)_2HV_{10}O_{27}]^-$ can be viewed as a dehydrated form of $[(TBA)_2H_3V_{10}O_{28}]^-$ after losing one water molecule. The dehydration phenomena of POM clusters in mass spectrometry has previously been reported for other polyoxometalate species.[11]

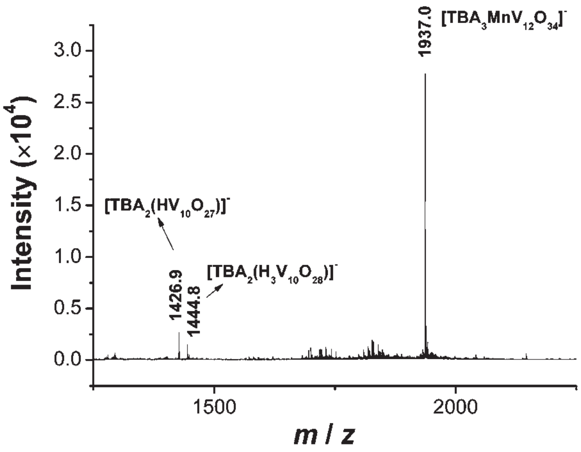

Fig. 3 The negative ion mode mass spectrum of the product isolated from the reaction of $K_7[Mn^{IV}V_{13}O_{38}]\cdot 18H_2O$ and TBABr in acetonitrile, showing the species related to $[MnV_{12}O_{34}]^{4-}$ and $[H_3V_{10}O_{28}]^{3-}$.

From our results, we can clearly identify the effect that substituting the potassium ions with large organic cations has on the stability of the dimeric $[K_2(MnV_{11}O_{32})_2]^{8-}$ species. It is widely accepted in POM chemistry that alkali metal cations, such as K^+ and Na^+, have a high affinity for both the bridging and terminal oxo-groups of polyoxoanions and frequently associate with them as $M^+(H_2O)_n$ units. On the other hand, large organic cations, such as TBA^+ and TPA^+, are much poorer electron acceptors and thus unable to form directional covalent or coordination bonds to POM clusters. Rather, organic cations are generally hydrophobic owing to their largely aliphatic nature, preferring instead to associate with the polyoxoanions through an extended network of weak electrostatic interactions. Crucially, as evident in the structure of $[K_2(MnV_{11}O_{32})_2]^{8-}$ (see Fig. 4), the K^+ ions play a vital role in stabilising the structure of the dimer, linking the two undecavanadate units through coordination to two terminal oxo-groups on one anion and a bridging μ_2-oxo atom on the other. When these are exchanged for TBA^+ or TPA^+, the dimeric unit is no longer stable in the absence of the bridging alkali metals and undergoes a spontaneous transformation into the discrete, higher symmetric dodecavanadate form *via* incorporation of an additional $\{VO_2\}$ unit, which 'closes' and thus stabilises the open V_4-face of the undecavanadate fragment. Interestingly, the higher symmetric triskaidecavanadate cluster, whilst monomeric, is also heavily stabilised by the presence of K^+ ions, which associate closely to the four V_4-faces of the clusters pseudo-cubic core (see Fig. S2†). The exchange of these stabilising metal ions for non-coordinating organic cations leads to the

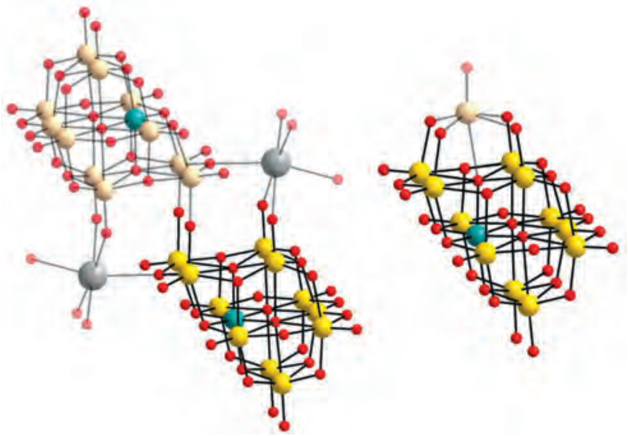

Fig. 4 Ball and stick models showing a comparison between the structure of the K$^+$ stabilised $[K_2(MnV_{11}O_{32})_2]^{8-}$ dimer[14,15] (left) and compound **1** (right). The undecavanadate building unit common to both compounds has been highlighted in each case. Colour code: V = yellow/tan, Mn = teal, K = grey, O = red.

decomposition of the cluster into the lower symmetry, but fundamentally more stable, dodecavanadate species in addition to decavanadate as a minor product. The introduction of non-coordinating organic cations is therefore the key driving force in the formation of the hitherto unreported dodecavanadomanganate species.

Cyclic voltammetry of **1** in acetonitrile over the potential range +1800 to −1500 mV at a scan rate of 10 mV s^{-1} in the direction of the negative region showed three quasi-reversible redox waves with the mean peak potentials ($E_{1/2} = (E_{pa} + E_{pc})/2$) located at −0.98 V, −0.54 V and 0.16 V, respectively, attributed to the formation of mixed-valence V^{V}/V^{IV} species (Fig. S3†).[21,22] The reduction waves of the Mn^{IV} centres are shaded by the V-centered redox processes. When the scan rate was increased to values higher than 50 mV s^{-1} it was possible to observe an ill-defined redox wave centered at −0.10 V, which was attributed to a Mn^{IV} → Mn^{II} reduction, whilst on potential reversal we observed the re-oxidation of Mn^{II} to Mn^{III} at + 0.50 V. Various examples have been described previously in the literature for the oxidation pathways of Mn centers in POMs, reported under a variety of situations and including important differences in potential locations.[23] As the scan rate was varied from slow to fast, the cathodic peak potentials shifted towards the negative direction and the corresponding anodic peak potentials shifted towards the positive direction leading to a gradual increase of peak-to-peak separation. It should be noted that when scan rates were lower than 100 mV s^{-1} the cathodic peak currents were proportional to the scan rates (Fig. S4†), indicating that the redox processes are surface controlled. At scan rates higher than 100 mV s^{-1}, the cathodic peak currents were proportional to the square root of the scan rates, suggesting that the redox processes were diffusion controlled.

Thermogravimetric analysis of **1** exhibits a three-step weight loss that correlates with the loss of various components of the crystal structure (Fig. S5†). The initial weight loss of 3.0% (calculated 3.6%) over the temperature range of 30–150 °C accounts for the loss of the two solvent acetonitrile molecules. The second decomposition process is associated with the loss of all TBA cations (41.7%, calculated 42.6%) present in the structure between 150 and 355 °C. The final weight loss corresponds to the decomposition of the metal oxide under a N_2 atmosphere. DSC of **1** also agrees with the loss of solvent at 150 °C and the loss of TBA at 317 °C.

In summary, the successful isolation of compound **1** clearly demonstrates the important role of the cations in the assembly process of POM clusters. Following the reaction of $K_{10}[(Mn^{IV}V_{11}O_{32})_2]$ with TBABr, **1** can be isolated in high purity whilst reacting $K_7[Mn^{IV}V_{13}O_{38}]$ with TBABr led to the formation of **1** as the major product. This simple synthetic methodology is a promising concept that can be readily extended to other polyoxometalate systems, particularly those in which alkali metal cations play a key role in stabilising the overall structure. Furthermore, high resolution, soft ionization mass spectrometry is proven to be a powerful means of exploring the identity of POM cluster species in solution.

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Notes and references

‡ Synthesis of $[(n\text{-}C_4H_9)_4N]_4[Mn^{IV}V_{12}O_{34}]\cdot 2CH_3CN$ (**1**): 3.00 g (1 mmol) of $K_{10}[(Mn^{IV}V_{11}O_{32})_2]\cdot 20H_2O$ was dissolved in 20 ml water. A prepared solution of TBABr (3.21 g, 10 mmol, in 20 ml water) was then added and the resultant slurry was stirred for a further 30 min. The mixture was then filtered and the yellow solid was collected and dried under vacuum overnight. Dark red single crystals could be obtained by diffusion of diethyl ether into an acetonitrile solution of **1**. (Yield = 2.0 g, 0.88 mmol, 44% based on $K_{10}[(Mn^{IV}V_{11}O_{32})_2]\cdot 20H_2O$) Elemental analysis calcd (%) for $C_{68}H_{150}N_6MnO_{34}V_{12}$: C 36.10, H 6.68, N 3.72; found: C 36.13, H 6.47, N 3.70. Characteristic IR bands (KBr): 3433 (br), 2960 (s), 2932 (m), 2871 (m), 1631 (w), 1480 (s), 1378 (w), 1309 (w), 1245 (w), 1151 (w), 992 (s), 860 (s), 756 (s), 577 (s), 450 (m), 388 (s) cm^{-1}. Crystallographic data: $(C_{16}H_{36}N)_4[MnV_{12}O_{34}]\cdot 2CH_3CN$, M_r = 2262.16 g mol^{-1}, monoclinic, space group $P2_1/n$, a = 27.2287(4), b = 42.8083(5), c = 34.1399(4) Å, β = 102.0660(10)°, V = 38914.8(9) Å^3, Z = 16, μ(Mo-Kα) = 1.296 mm^{-1}. Final R_1 = 0.0806 and wR_2 = 0.2353 (all data). Further details on the crystal structure investigation may be obtained from the ESI.†

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