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

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Experimental

The starting material $K_{10}[(Mn^{IV}V_{11}O_{32})_2] \cdot 20H_2O$ was synthesized according to the literature procedure.¹

Synthesis of $[(n-C_4H_9)_4N]_4[Mn^{IV}V_{12}O_{34}]$ (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 30min. 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 $K_{10}[(Mn^{IV}V_{11}O_{32})_2]$) Elemental analysis calcd (%) for the dehydrated material, $C_{68}H_{150}N_6MnO_{34}V_{12}$: 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: $(C_{16}H_{36}N)_4[MnV_{12}O_{34}] \cdot 2CH_3CN$, $Mr = 2262.16 \text{ g}\cdot\text{mol}^{-1}$, monoclinic, space group $P2_1/n$, a = 27.2287(4), b = 42.8083(5), c = 34.1399(4) Å, $\beta = 102.0660(10)^{\circ}$, V = 38914.8(9) Å³, Z = 16, $\mu(Mo-K\alpha) = 1.296 \text{ mm}^{-1}$. Final $R_1 = 0.0806$ and $wR_2 = 0.2353$ (all data).

X-Ray Single Crystal Diffraction: A single crystal was selected and mounted onto the end of a thin glass fiber using Fomblin oil. X-ray diffraction intensity data were measured at 150(2) K on an Oxford Gemini Ultra A diffractometer [λ (Mo-K α) = 0.7107 Å]. Structure solution and refinement was carried out using SHELXS-97² and SHELXL-97² via WinGX.³ Corrections for incident and diffracted beam absorption effects were applied using empirical methods.⁴

Microanalysis: Carbon, nitrogen and hydrogen content were determined by the microanalysis services within the School of Chemistry, University of Glasgow using an EA 1110 CHN, CE-440 Elemental Analyser.

Fourier Transform Infrared (FT-IR) Spectroscopy: 1 was prepared as a KBr pellet and a FT-IR spectrum was collected in transmission mode using a JASCO FT-IR-4100 spectrometer.

Mass Spectrometry: Electrospray ionisation (ESI) and cryospray ionisation (CSI) measurements were carried out on a Bruker MicrOTOF-Q spectrometer operating in negative ion mode. Solutions were prepared by dissolving the dried powder of the relevant sample in HPLC grade acetonitrile to a concentration of *ca.* 1x10⁻⁵ M. The spectra presented in figures 2 and 3 were conducted using CSI-MS via attachment of a separate Bruker cryospray unit, whereas the spectrum shown in figure S1 was conducted using standard ESI-MS. For all measurements the settings applied were; capillary tip voltage: 4kV, end plate offset: -500V, funnel 1 RF: 300 Vpp, funnel 2 RF: 400 Vpp, hexapole RF: 400 Vpp. All data was processed using Bruker Daltonics Data Analysis 4.0 software.

Electrochemical Measurements: The solutions were deaerated thoroughly for at least 30 min with pure nitrogen and kept under a positive pressure of this gas during the experiment. The source, mounting and polishing of the glassy carbon (GC) electrodes have been described previously.⁵ The glassy carbon samples had a diameter of 3 mm. Potentials are quoted against a Ag/AgCl electrode. Platinum gauze of large surface area was used as the counter electrode. All experiments were performed at room temperature.

Thermogravimetric Analysis (TGA): TGA was performed on a TA Instruments Q 500 Thermogravimetric Analyzer under nitrogen flow at a heating rate of 10 °C min-1 in a platinum pan.

Differential Scanning Calorimetry (DSC): DSC analysis was performed on a TA Instruments Q 200 calorimeter under nitrogen flow at a heating rate of 20 °C min-1.





Fig. S2: Structure of the triskaidecavanadomanganate cluster $K_7[MnV_{13}O_{38}]$,⁶ clearly showing the stabilising effect of the K⁺ cations associated with the four faces of the pseudo-cubic {V₁₁} core. The "V₄-face" to which the K⁺ ions coordinate has been highlighted with a plane below. It should also be noted that whilst the structure, as depicted, appears to contain 14 V atoms, the tan coloured V positions are only partially occupied yielding an overall stoichiometry of [MnV₁₃O₃₈]⁷⁻. Colour code: V = Yellow/Tan, Mn = Teal, K = Grey, O = Red.



Fig. S3: Cyclic voltammetry of **1** (1.0 mM) in acetonitrile (with 0.1 M TBAPF₆ as electrolyte) referenced to Ag/AgCl at a scan rate of of 10, 50 and 100 mV s⁻¹ (inner to outer).



Fig. S4: Plots showing that peak current is proportional to scan rate from 10 to 100 mv s⁻¹ (left) and that peak current is directionally proportional to (scan rate)^{1/2} from 200 to 400 mv s⁻¹ (right).





Fig. S5: The TGA and DSC curves for compound 1 in the temperature range of 30-600 °C.

Fig. S6: IR spectrum of compound **1** with characteristic bands at 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) and 388(s) cm⁻¹.



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