Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

A novel manganese-doped large polyoxotitanate nanocluster

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Experimental Section:

Synthesis of $Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$. All chemicals and solvent were obtained from commercial sources and used as received: Titanium(IV) ethoxide (99+ %) was purchased from Alfa Aesar; manganese(III) acetate dihydrate (97 %) was purchased from Aldrich Chem. Co.; Ammonium bromide was purchased from FISHER SCIENTIFIC COMPANY; ethanol (200 proof, anhydrous, ≥ 99.5 %) was purchased from SIGMA-ALDRICH. All compounds containing titanium were stored and handled in a glove-box under a nitrogen atmosphere.

To a Teflon-lined Parr bomb with a capacity of 23 mL were added titanium(IV) ethoxide (1.09 g, 4.77 mmol), manganese(III) acetate dihydrate (0.07 g, 0.25 mmol), ammonium bromide (0.05 g, 0.50 mmol) and ethanol (5.0 mL) in the glove-box. After the mixture was stirred for about 5 minutes, the bomb was sealed, then placed in a 150 °C oven for 66 hours. After the oven was cooled to room temperature, pale-yellow plate-shaped crystals of $Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$ were generated. They were collected by filtration, washed with ethanol and dried in the glove-box. Yield: 58.7 mg (8.9 % based on titanium(IV) ethoxide). The ^1H NMR spectrum of $Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$ in $CDCl_3$ is shown in Fig. S6.

Structure Determination of $Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$. X-ray Diffraction data on $Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$ were collected at 90 K on a *Bruker* APEX II ULTRA MO TXS TURBO diffractometer (MoK_α radiation, λ = 0.71073 Å), equipped with Helios optics and an Oxford Cryosystems nitrogen flow apparatus. Data integration was carried

out using *SAINT V7.68.*[1] The associated program *SADABS* was used for reflection spot size optimization and absorption corrections. Full and partial reflections were merged in SORTAV.[2] The structure was solved by direct methods and refined by least-squares methods against F^2 using *SHELX* package.[3] Non-hydrogen atoms were refined anisotropically; all hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. Several of the ethyl groups attached to $Ti_{28}MnO_{38}(OEt)_{40}H_2$ are disordered. One of the titanium atoms is three-fold disordered. The sites Ti1, Ti1A and Ti1B (Fig. S3) have 80%, 15% and 5% occupancy respectively, leading to pseudo-C_{3v} symmetry of the cluster. Only ethoxide ligands attached directly to the Ti1 site have been included in the model and given appropriate occupancies.

Charge neutrality of the cluster requires the presence of two hydrogen atoms attached to peripheral core oxygen sites. As these hydrogen atoms could not be located in the difference maps they were not included in the refined model. Crystal data as well as details of data collection and refinement are in given in Table S1. Further details can be found in CCDC-970095 which can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or deposit@ccdc.cam.uk (the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033).

Table S1 Crystal data and details of data collection and refinement for $Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$.

Compound	$Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$
Chemical formula	$C_{81.2}H_{206}O_{78.6}MnTi_{28}$
Formula weight	3836.60
Crystal system	Triclinic
Space group	$P\bar{1}$
a / Å	16.4916(14)
b / Å	16.3890(14)
c / Å	28.717(2)
α / °	89.854(2)
β / °	97.370(2)
γ / °	107.859(2)
V / Å^3	7321.1(10)
Z	2
T / K	90(2)
F(000)	3926
μ (Mo Kα, mm^{-1})	1.604
Total # of reflections	124449
Unique # of reflections	28727
No. of parameters	1896
R [a]	0.0702
ωR[b]	0.1572
GOF [c]	1.055

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR = (\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2)^{1/2}$. [c] $GOF = (\Sigma[w((F_o^2-F_c^2)^2)/(n-p))^{1/2}$, where n = number of reflections, p = numbers of variables.

Table S2 Mn-O or Ti(fourcoordinated)-O bond lengths and their average values in $Ti_{28}MnO_{38}(OEt)_{40}H_2$·EtOH, $Ti_{28}Ln$ (Ln = La, Ce), $Ti_{28.5}AO_{38}(OEt)_{39}$ (A= Li, Na), $Ti_{17}O_{24}(O^iPr)_{20}$,[4] and $Ti_{14}MnO_{16}(OEt)_{28}H_2$.

Polyoxotitanate nanocluster	Mn-O or Ti(fourcoordinated)-O bond lengths (Å)	Average of Mn-O or Ti(fourcoordinated)-O bond lengths (Å)
$Ti_{28}MnO_{38}(OEt)_{40}H_2$	1.988(4) 2.006(4) 2.007(4) 2.013(4)	2.004(4)
$Ti_{28.5}LiO_{38}(OEt)_{39}$[5]	1.913(4) 1.919(4) 1.930(4) 1.993(4)	1.939(4)
$Ti_{28.5}NaO_{38}(OEt)_{39}$[5]	1.829(4) 1.846(4) 1.852(4) 1.856(4)	1.846(4)
$[Ti_{28}LaO_{36}(OH)_2(OEt)_{40}]Cl$[6]	1.868(5) 1.938(6) 1.995(5) 1.998(6)	1.950(6)
$[Ti_{28}CeO_{36}(OH)2(OEt)_{40}]Cl$[6]	1.843(6) 1.928(6) 1.992(6) 2.012(6)	1.944(6)
$Ti_{17}O_{24}(O^iPr)_{20}$[4]	1.800(10) 1.807(9) 1.820(8) 1.820(10)	1.812(9)
$Ti_{14}MnO_{16}(OEt)_{28}H_2$[7]	2.0569(11) 2.0570(11)	2.0570(11)

X-ray Spectroscopy of the title compound.

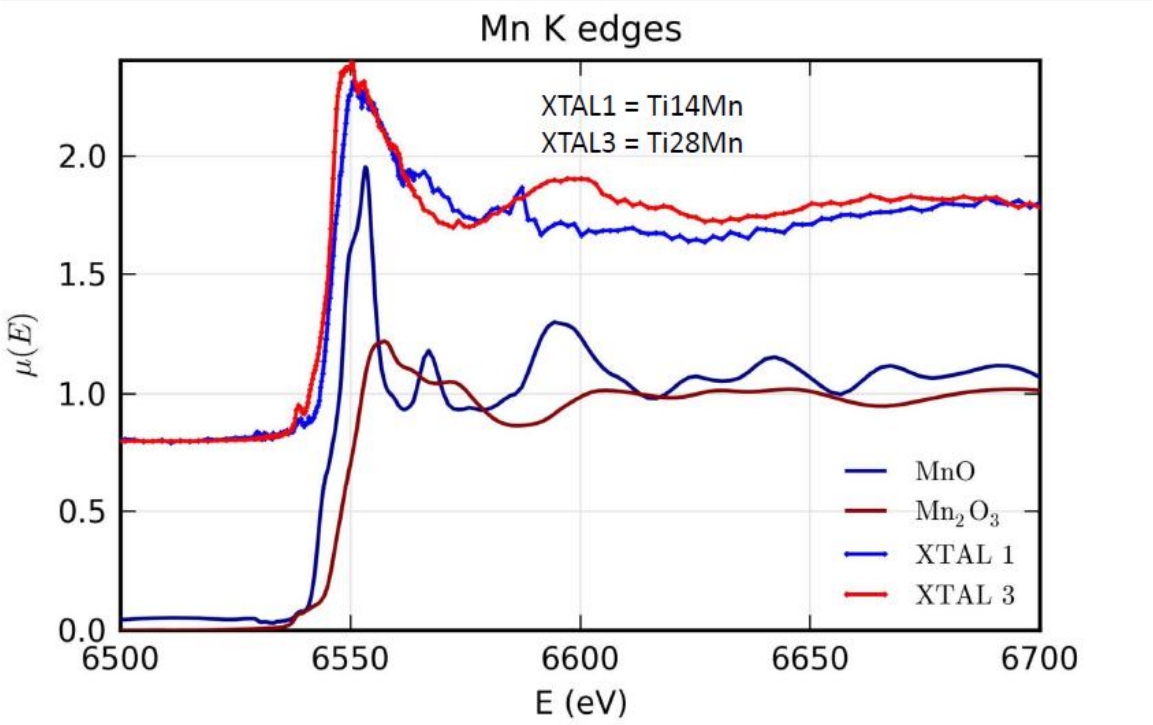
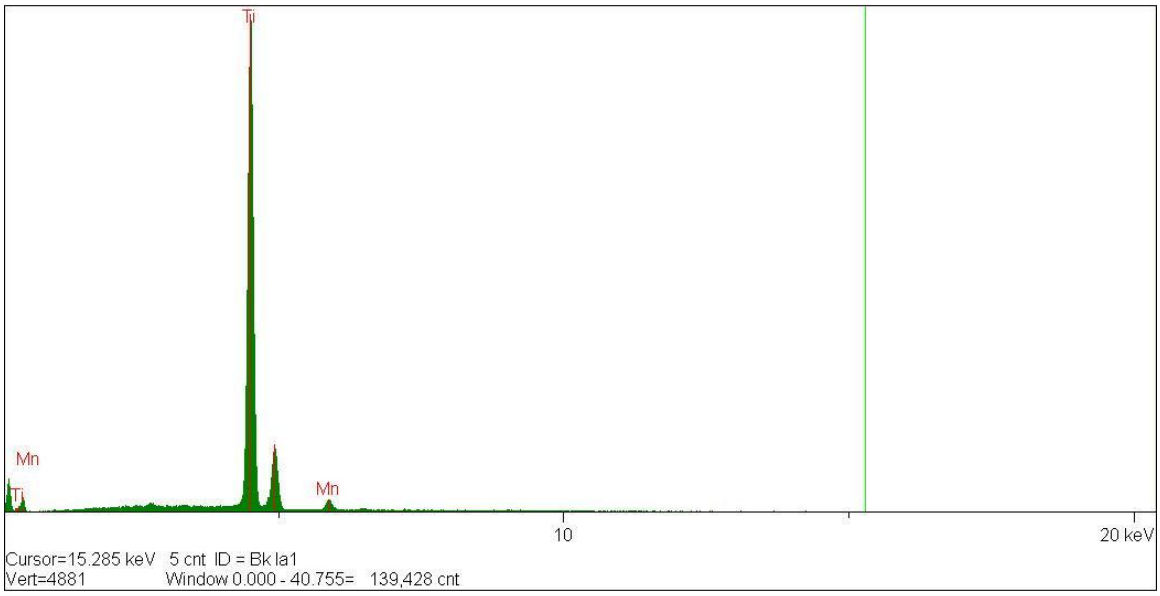


Fig. S1 The XAS (X-ray Absorption Structure) spectra of $Mn(CH_3COO)_3 \cdot 4H_2O$, $MnBr_2 \cdot 4H_2O$ (both for calibration), $Ti_{14}MnO_{16}(OEt)_{28}H_2$, $Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$. The Mn^{2+} absorption edges are shifted to lower binding energies.



Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
Ti	Ka	2,435.15	20.023	96.442	95.938	wt.%	
Mn	Ka	58.36	3.741	3.558	4.062	wt.%	
				100.000	100.000	wt.%	Total

kV	30.0
Takeoff Angle	45.0°
Elapsed Livetime	25.0

Fig. S2 EDS spectrum of $Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$.

Structure Diagrams.

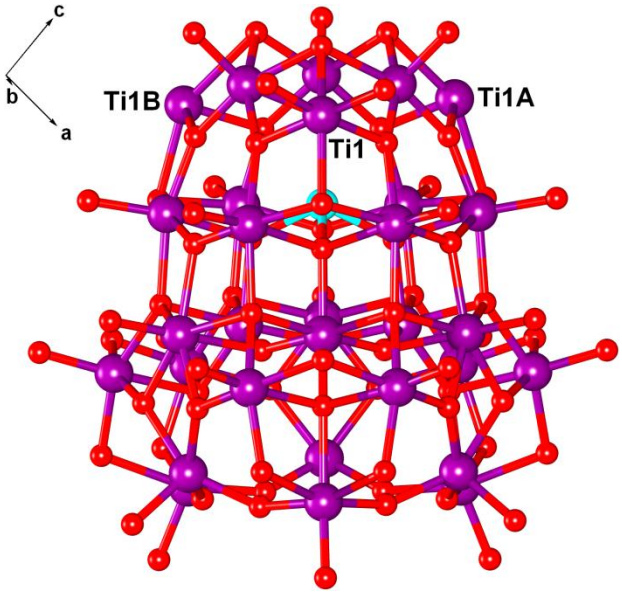


Fig. S3 The Ti1 atom of $Ti_{28}MnO_{38}(OEt)_{40}H_2$ cluster is disordered over three positions with the occupancy of 80 % (Ti1), 15 % (Ti1A) and 5 % (Ti1B), respectively. Ethyl groups are omitted for clarity.

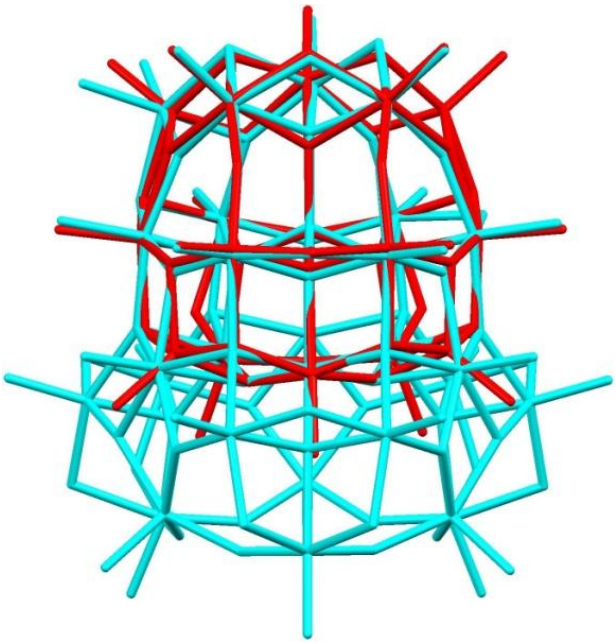


Fig.S4 Structure overlay of $Ti_{28}MnO_{38}(OEt)_{40}H_2$ (cyan) and $Ti_{17}O_{24}(O^iPr)_{20}$ (red). Alkyl groups are omitted for clarity.

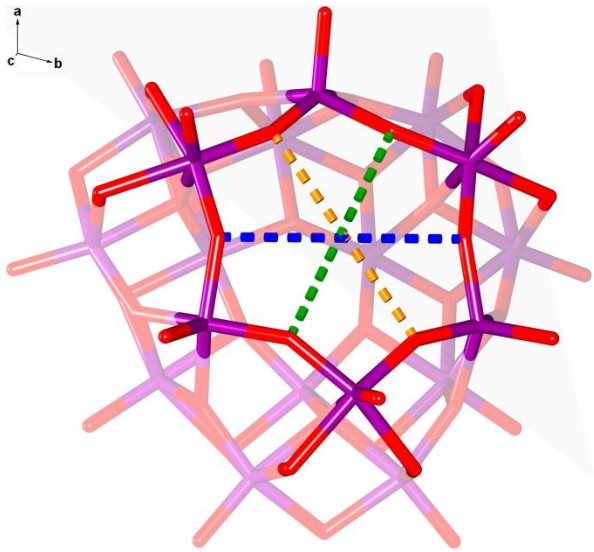


Fig. S5 Three O···O cross-ring distances (blue, green and orange dashed lines) of the crown configurationin the $Ti_{28}MnO_{38}(OEt)_{40}H_2$ cluster.

NMR Spectrum of the Title Compound.

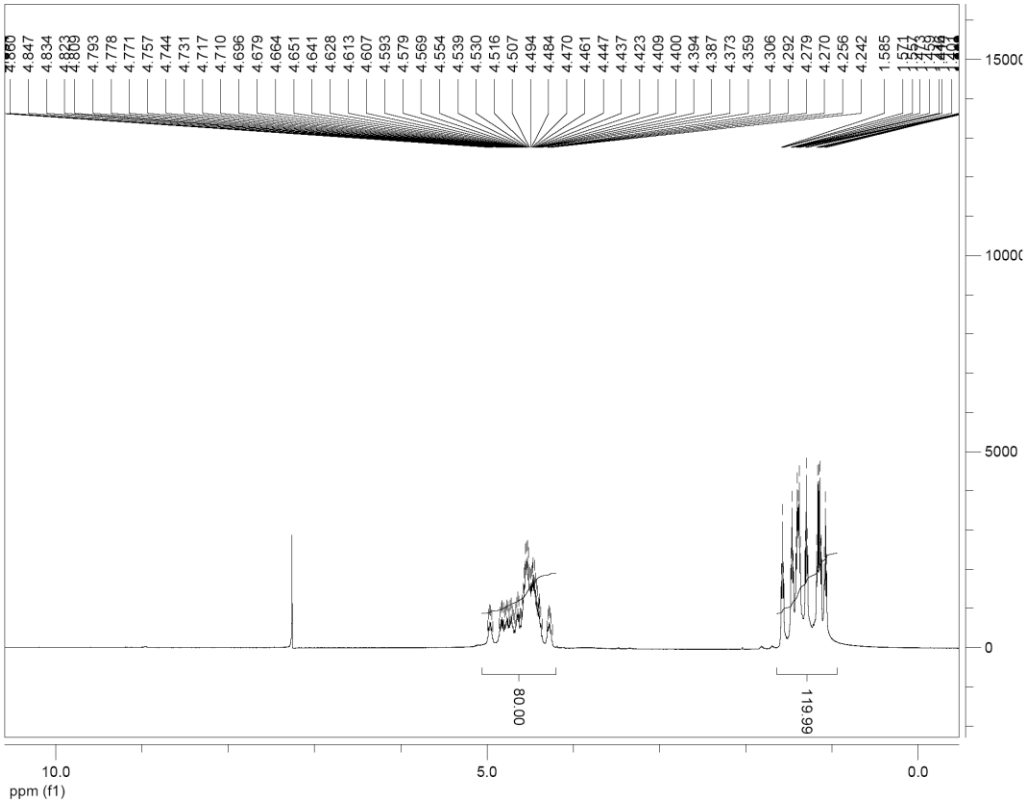


Fig. S6 Solution ^{1}H NMR spectrum of $Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$ in $CDCl_3$. The peaks of ethanol are minor in the ^{1}H NMR solution spectrum.

Powder Pattern after Reflectance Spectroscopy and Comparison with Anatase and Calculated Pattern based on the Single-Crystal Data.

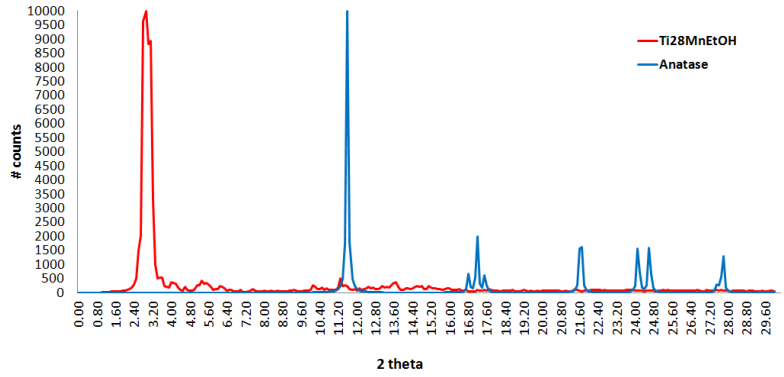


Fig. S7. Calculated powder patterns of anatase (blue) and of $Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$ (red) (MoKα radiation). The reported powder pattern of Mn-doped anatase has the same maxima as those for anatase shown here.[8]

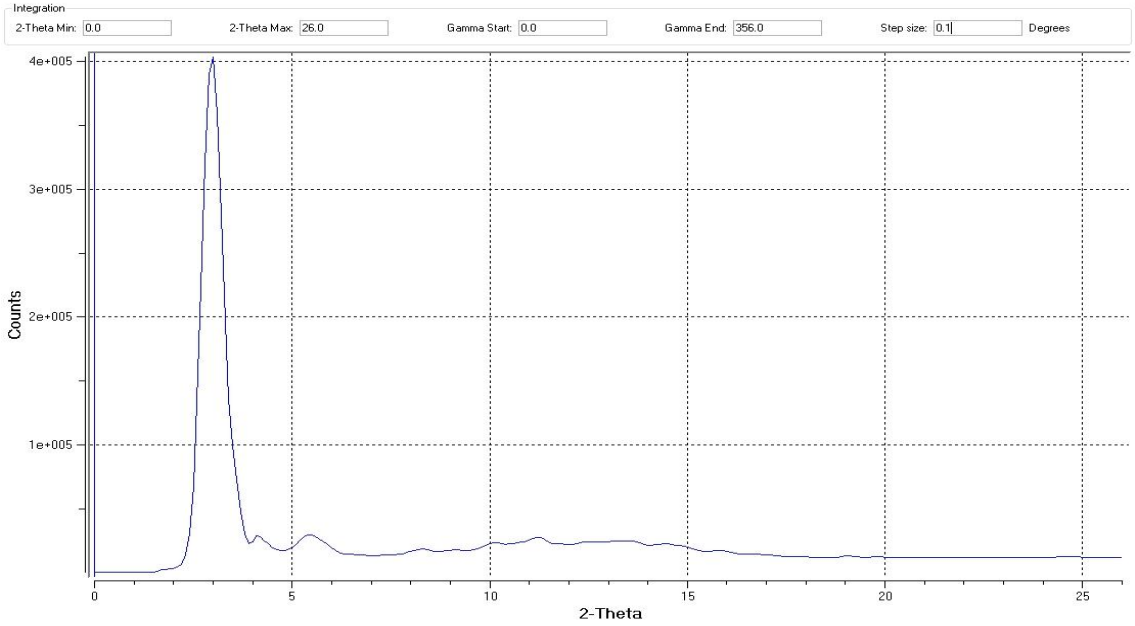


Fig. S8. Experimental powder pattern of $Ti_{28}MnO_{38}(OEt)_{40}H_2 \cdot EtOH$, measured after reflectance spectroscopy (APEX II ULTRA MO TXS TURBO diffractometer , MoKα radiation).

1. *SMART and SAINTPLUS - Area Detector Control and Integration Software*, *version 6.01*, Bruker AXS: Madison, WI, 1999.
2. (a) Blessing, R. H., Data reduction and error analysis for accurate single crystal diffraction intensities. *Crystallogr. Rev.* **1987,** *1* (1), 3-58; (b) Blessing, R., DREADD - data reduction and error analysis for single-crystal diffractometer data. *J. Appl. Crystallogr.* **1989,** *22* (4), 396-397.
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