Supporting Information

High symmetry superoctahedron cluster $[Mn^{III}_{18}O_{14}]^{26+}$ from the use of N,N,N',N'-Tetrakis(2-hydroxyethyl)ethylenediamine

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Contents

Synthesis of **1**:

The reaction of copper powder (0.660 g, 11 mmol), $Mn(ClO_4)_2 \cdot 6H_2O$ (1.874 g, 3 mmol), H_4edte (0.772 g, 3 mmol), NaOH (0.561 g, 12 mmol) and sodium dicyanamide (0.541 g, 6 mmol)in a mixed solution by N,N'-dimethylformamide (DMF) (10 mL) and methyl alcohol (20 mL) at 80 °C gave a dark green solution from which dark block crystals of **1** were slowly deposited after several months. Yield, 30%. Anal. Calc. for $C_{62}H_{122}Mn_{18}N_{12}O_{42}$ (**1**) found: C 27.58, H 4.61, N 6.19; calcd: C 27.62, H 4.56, N 6.23. IR for **1**: 3429, 2841, 2140, 1658, 1461, 1363, 945, 640 cm^{-1}.

X-ray Crystallography

The Diffraction data for complex **1** was recorded on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296 K. Processing data were accomplished with use of the program *SAINT*;[1] an absorption correction based on symmetry equivalent reflections was applied using the *SADABS* program. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 with *SHELXTL* program package.[2] The edte ligand was disordered at two positions with 50:50% refined occupancies. All non-hydrogen atoms were refined with anisotropic displacement parameters. The CCDC reference numbers are 926202 for crystal **1**. The selected bond lengths and bond angels are provided in Table **S1**.

Table S1. Bond distances (Å) and angles (°) in **1.**

Mn(1)-O(1)	1.922(4)	Mn(2)-O(5'*b*)	2.108(7)
Mn(1)-O(2)	1.926(6)	Mn(2)-O(5*b*)	2.108(7)
Mn(1)-O(4'*a*)	2.054(8)	Mn(2)-O(3)	2.190(7)
Mn(1)-O(4*a*)	2.054(8)	Mn(3)-O(5)	1.935(7)
Mn(1)-O(3*a*)	2.054(7)	Mn(3)-O(4)	1.943(8)
Mn(1)-O(6)	2.075(7)	Mn(3)-O(6)	1.953(7)
Mn(1)-O(3)	2.119(7)	Mn(3)-O(7)	1.981(7)
Mn(2)-O(2*d*)	1.923(6)	Mn(3)-O(3)	2.277(6)
Mn(2)-O(2)	1.926(6)	Mn(3)-N(2')	2.39(2)
Mn(2)-O(7)	1.981(7)	Mn(3)-N(2)	2.431(19)
Mn(2)-O(3*b*)	2.033(7)	Mn(3)-N(1')	2.47(3)
O(1)-Mn(1)-O(2)	163.7(3)	O(5'*b*)-Mn(2)-O(5*b*)	0.0(4)

O(1)-Mn(1)-O(4'*a*)	94.6(3)	O(2*d*)-Mn(2)-O(3)	83.1(2)
O(2)-Mn(1)-O(4'*a*)	95.3(3)	O(2)-Mn(2)-O(3)	84.3(3)
O(1)-Mn(1)-O(4*a*)	94.6(3)	O(7)-Mn(2)-O(3)	79.9(3)
O(2)-Mn(1)-O(4*a*)	95.3(3)	O(3*b*)-Mn(2)-O(3)	96.6(3)
O(4'*a*)-Mn(1)-O(4*a*)	0.0(4)	O(5'*b*)-Mn(2)-O(3)	179.4(3)
O(1)-Mn(1)-O(3*a*)	85.1(3)	O(5*b*)-Mn(2)-O(3)	179.4(3)
O(2)-Mn(1)-O(3*a*)	83.6(3)	O(5)-Mn(3)-O(4)	88.9(3)
O(4'*a*)-Mn(1)-O(3*a*)	81.0(3)	O(5)-Mn(3)-O(6)	162.9(3)
O(4*a*)-Mn(1)-O(3*a*)	81.0(3)	O(4)-Mn(3)-O(6)	87.4(3)
O(1)-Mn(1)-O(6)	95.0(3)	O(5)-Mn(3)-O(7)	87.8(3)
O(2)-Mn(1)-O(6)	96.2(3)	O(4)-Mn(3)-O(7)	155.8(3)
O(4'*a*)-Mn(1)-O(6)	99.7(3)	O(6)-Mn(3)-O(7)	88.8(3)
O(4*a*)-Mn(1)-O(6)	99.7(3)	O(5)-Mn(3)-O(3)	81.4(3)
O(3*a*)-Mn(1)-O(6)	179.3(3)	O(4)-Mn(3)-O(3)	78.0(3)
O(1)-Mn(1)-O(3)	83.3(3)	O(6)-Mn(3)-O(3)	81.5(3)
O(2)-Mn(1)-O(3)	86.3(3)	O(7)-Mn(3)-O(3)	77.8(3)
O(4'*a*)-Mn(1)-O(3)	176.9(3)	O(5)-Mn(3)-N(2')	83.4(8)
O(4*a*)-Mn(1)-O(3)	176.9(3)	O(4)-Mn(3)-N(2')	132.3(6)
O(3*a*)-Mn(1)-O(3)	96.5(3)	O(6)-Mn(3)-N(2')	111.3(8)
O(6)-Mn(1)-O(3)	82.8(3)	O(7)-Mn(3)-N(2')	71.0(5)
O(2*d*)-Mn(2)-O(2)	163.9(3)	O(3)-Mn(3)-N(2')	145.7(6)
O(2*d*)-Mn(2)-O(7)	93.8(3)	O(5)-Mn(3)-N(2)	116.7(6)
O(2)-Mn(2)-O(7)	93.8(3)	O(4)-Mn(3)-N(2)	129.8(6)
O(2*d*)-Mn(2)-O(3*b*)	84.2(3)	O(6)-Mn(3)-N(2)	78.0(6)
O(2)-Mn(2)-O(3*b*)	87.3(3)	O(7)-Mn(3)-N(2)	72.4(5)
O(7)-Mn(2)-O(3*b*)	176.2(3)	O(3)-Mn(3)-N(2)	143.9(5)
O(2*d*)-Mn(2)-O(5'*b*)	96.4(3)	N(2')-Mn(3)-N(2)	33.4(9)
O(2)-Mn(2)-O(5'*b*)	96.2(3)	O(5)-Mn(3)-N(1')	115.3(7)
O(7)-Mn(2)-O(5'*b*)	99.9(3)	O(4)-Mn(3)-N(1')	69.2(6)
O(3*b*)-Mn(2)-O(5'*b*)	83.5(3)	O(6)-Mn(3)-N(1')	78.8(7)
O(2*d*)-Mn(2)-O(5*b*)	96.4(3)	O(7)-Mn(3)-N(1')	133.2(6)
O(2)-Mn(2)-O(5*b*)	96.2(3)	O(3)-Mn(3)-N(1')	142.2(6)
O(7)-Mn(2)-O(5*b*)	99.9(3)	N(2')-Mn(3)-N(1')	72.0(8)
O(3*b*)-Mn(2)-O(5*b*)	83.5(3)	N(2)-Mn(3)-N(1')	61.0(8)

Symmetry codes: *(a)* $z+{}^{1}/_{2}, -x+{}^{3}/_{2}, -y+1$; *(b)* $y, z+{}^{1}/_{2}, -x+1$; *(d)* $-z+1, x, y-{}^{1}/_{2}$.

Table S2. Composition of the complex **1** by EDX Analysis.

Element	Atomic%
C	27.13
N	36.51
O	29.50
Na	0.39
Cl	0.82

Mn	5.64

Table S3. Peak Table for complex **1** by XPS.

Name	PP At. %
C1s	65.7
O1s	18.72
N1s	10.21
Mn2p	3.64
Cl2p	0.87
Na1s	0.87

Table S4. BVS for complex **1**.

Mn1	**3.241**		
Mn(1)-O(1)	0.699	Mn(1)-O(3*a*)	0.489
Mn(1)-O(2)	0.692	Mn(1)-O(6)	0.462
Mn(1)-O(4*a*)	0.489	Mn(1)-O(3)	0.410
Mn2	**3.266**		
Mn(2)-O(2*d*)	0.698	Mn(2)-O(3*b*)	0.518
Mn(2)-O(2)	0.692	Mn(2)-O(5*b*)	0.423
Mn(2)-O(7)	0.596	Mn(2)-O(3)	0.339
Mn3	**3.173**		
Mn(3)-O(5)	0.675	Mn(3)-O(3)	0.268
Mn(3)-O(4)	0.562	Mn(3)-N(2)	0.232
Mn(3)-O(6)	0.643	Mn(3)-N(1')	0.197
Mn(3)-O(7)	0.596		

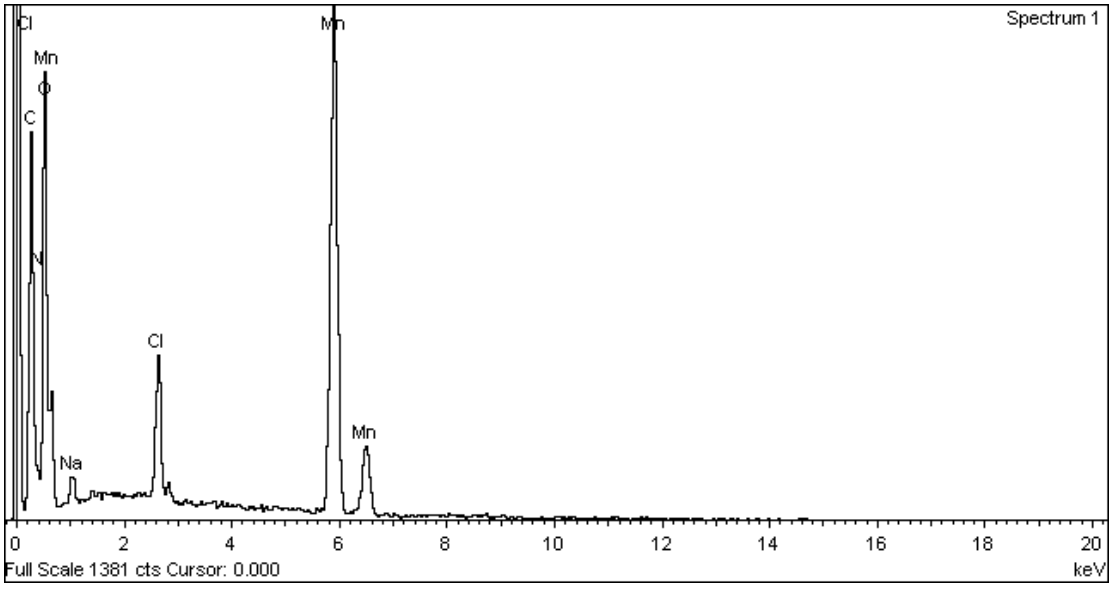

Figure S1 The EDX spectrum of the complex **1**.

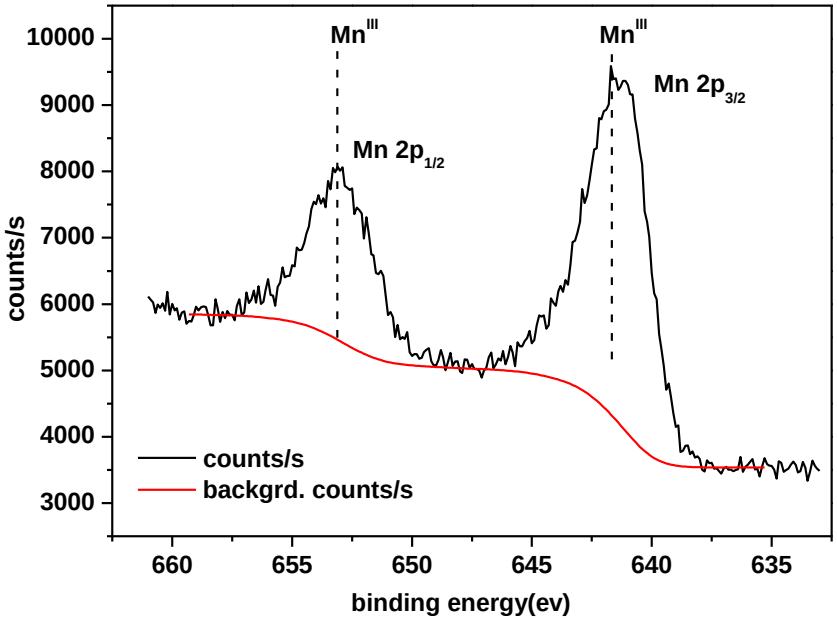

Figure S2. X-ray photoelectron spectrum of 1.
XPS peaks for 2*p* electrons consistent with a mixture of Mn^{III} (641 ev for $2p_{3/2}$, 653 ev for $2p_{1/2}$) oxidation states.[13]

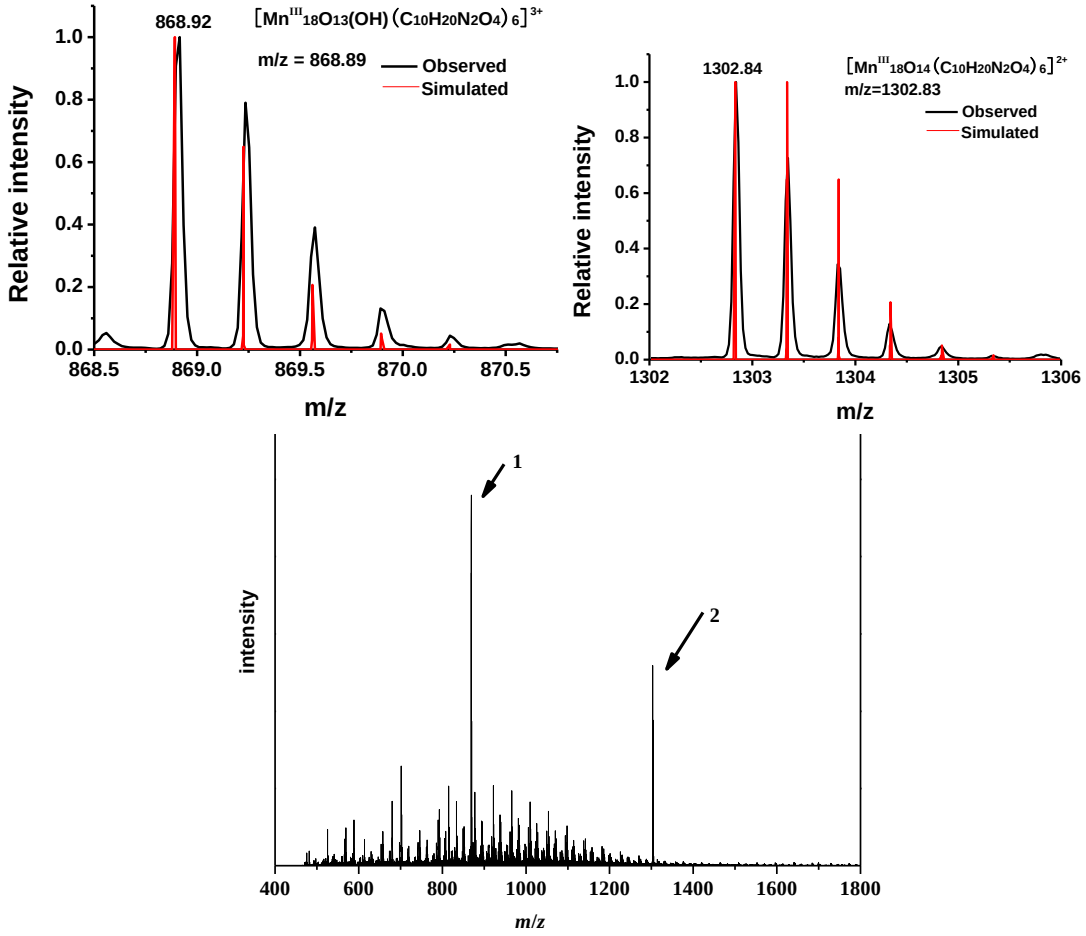

Figure S3. Electrospray ionization mass spectrometry (ESI-MS) for **1.**

Table S5. Peak assignment for **1.**

Assignment	***m/z***	**Formula**
1	868.9	$[Mn^{III}_{18}O_{13}(OH)(C_{10}H_{20}N_2O_4)_6]^{3+}$
2	1302.8	$[Mn^{III}_{18}O_{14}(C_{10}H_{20}N_2O_4)_6]^{2+}$

Electrospray mass spectrometry measurements were conducted using the ESI-MS attachment at 180°C. The methanol solution of Mn_{18} crystals was injected into the device at 180 mL h^{-1}. The mass spectrometer used for the measurements was a Bruker micro-TOFQ and the data were collected in positive ion mode. The spectrometer was previously calibrated with the standard tune mix to give a precision of ca. 2 ppm in the region of 500–5000 m/z. The end plate voltage was set to -500 V and the capillary to -4500 V. The collision cell was set to collision energy of a 10.0 eV z^{-1} with a gas flow rate at 25% of the maximum and the cell RF was set at 1600 Vpp.

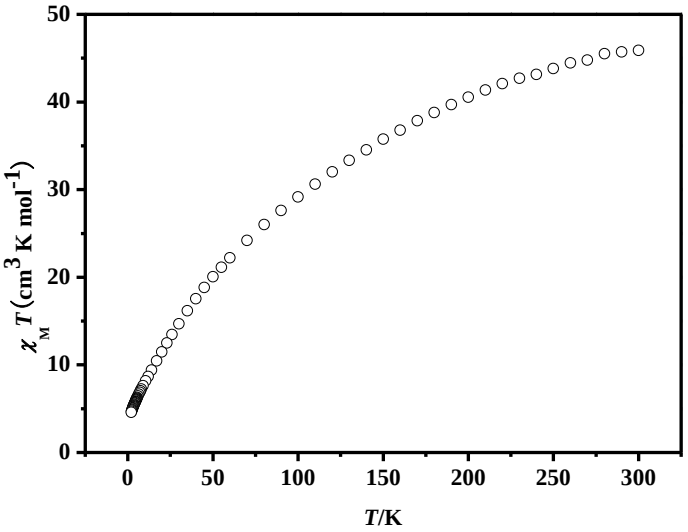

Figure S4. Temperature dependence of χT for **1** from 300−1.8 K measured in a field of 1 kOe.

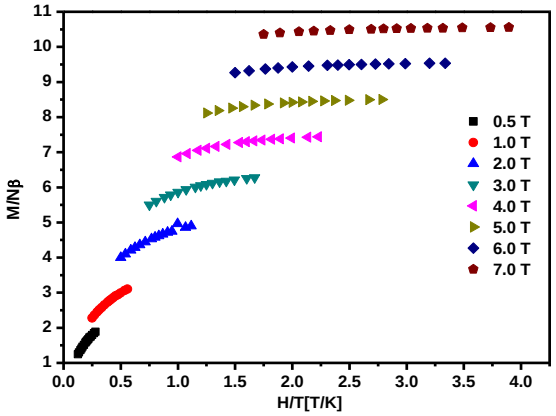

Figure S5. Plot of reduced magnetization ($M/N\beta$) versus H/T for 1 in the temperature

range of 1.8-7.0 K.

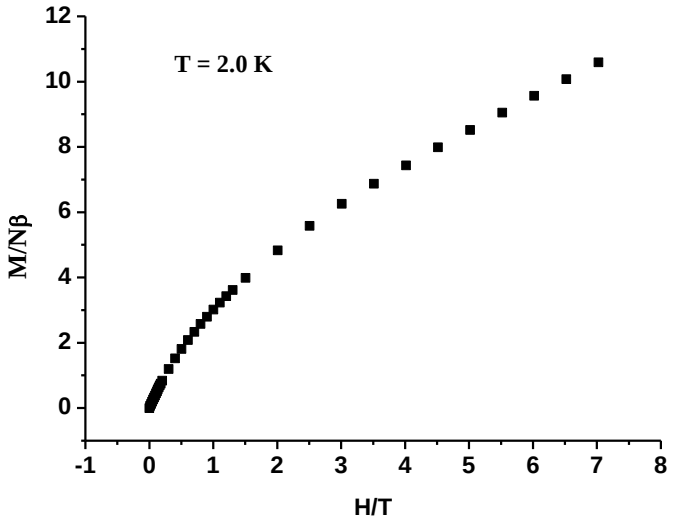

Figure S6. Magnetization data for **1** at 2 K measured from 0−7 T.

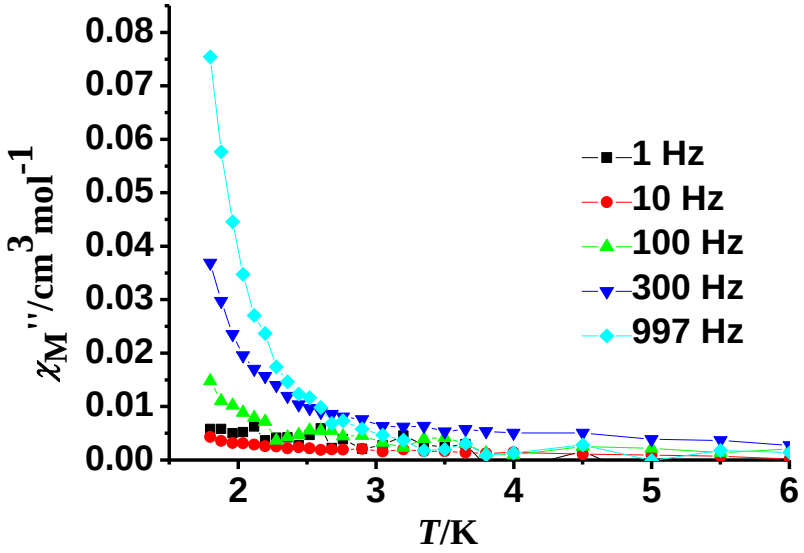

Figure S7. Ac magnetization data for **1** from 1.8-6.0 K.

Reference:

1 R.H. Blessing, *Acta Crystallogr.*, 1995, **A51**, 33.

2 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.