

# SUPPORTING INFORMATION

## **‘Molecular Nanoclusters’: A 2 nm-Sized {Mn<sub>29</sub>} Cluster with a Spherical Structure**

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## Experimental Section

**Synthesis.** All manipulations were performed under aerobic conditions using chemicals and solvents as received unless otherwise stated.  $\text{NBu}^n_4\text{MnO}_4$  was prepared as described elsewhere.<sup>1</sup>

*WARNING: Appropriate care should be taken in the use of  $\text{NBu}^n_4\text{MnO}_4$ , and readers are referred to the detailed warning given elsewhere.<sup>1</sup> Furthermore, azide salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times.*

**[ $\text{Mn}_{29}\text{O}_{24}(\text{N}_3)_{10}(\text{dma})_{28}$ ] (**1**).** To a stirred colorless solution of  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (0.54 g, 3.0 mmol) in  $\text{MeNO}_2/\text{dmaH}$  (15/3 mL) was added in small portions solid  $\text{NBu}^n_4\text{MnO}_4$  (0.36 g, 1.0 mmol), causing a rapid color change to dark brown. To this solution was added  $\text{Me}_3\text{SiN}_3$  (0.55 mL, 4.0 mmol) and the resulting dark red solution was stirred for 10 min, filtered, and the filtrate left undisturbed to concentrate slowly by evaporation. After twenty days, X-ray quality dark-brown crystals of **1** had appeared and were collected by filtration, washed with cold  $\text{MeNO}_2$  ( $2 \times 3$  mL) and dried in air; the yield was 25 %. Anal. Calcd for  $\text{1} \cdot 3\text{H}_2\text{O}$ : C, 32.17; H, 3.90; N, 8.04 %. Found: C, 32.01; H, 3.77; N, 8.24 %. Selected IR data ( $\text{cm}^{-1}$ ): 2908 (m), 2071 (2), 1637 (m), 1551 (m), 1490 (m), 1401 (vs), 1310 (s), 1261 (m), 1183 (m), 1074 (m), 976 (w), 861 (m), 835 (m), 750 (m), 678 (sb), 640 (s), 577 (s), 482 (w), 411 (m).

**Synthetic discussion.** The use of  $\text{Me}_3\text{SiN}_3$  as an excellent and unique precursor for the delivery of azido-bridged cluster compounds with unprecedented structural motifs and interesting magnetic properties has been recently demonstrated by the synthesis of the organic chelate ligand-free compounds  $[\text{Co}^{\text{II}}_7(\text{N}_3)_{12}(\text{MeCN})_{12}](\text{ClO}_4)_2$ ,  $[\text{Ni}^{\text{II}}_7(\text{N}_3)_{12}(\text{MeCN})_{12}](\text{ClO}_4)_2$  and  $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{N}_3)_5(\text{MeCN})_2]_n$  (see reference 12 in the main article). The obvious advantage of

$\text{Me}_3\text{SiN}_3$  is its solubility, and facile release of  $\text{N}_3^-$ .  $\text{NaN}_3$  and  $\text{KN}_3$  salts are not very soluble, and organic azides would be dangerous. Although the mechanism of clusters' formation is difficult to be rationalized, we also believe that the released in solution  $\text{Me}_3\text{Si}^+$  cations can abstract the existed  $\text{OH}^-$  groups (most likely resulting from  $\text{H}_2\text{O}$ -containing solvents and starting materials), thus allowing the  $\text{N}_3^-$  groups to coordinate and bridge the metal centers.

### Single-crystal X-ray diffraction studies

A crystal of complex **1** was selected and mounted on a cryoloop using inert oil.<sup>2</sup> Diffraction data were collected at 150.0(2) K on a Bruker X8 Kappa APEX II Charge-Coupled Device (CCD) area detector diffractometer controlled by the APEX2 software package<sup>3</sup> (MoK $\alpha$  graphite-monochromated radiation,  $\lambda = 0.71073$  Å), and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely with the software interface Cryopad.<sup>4</sup> Images were processed with the software SAINT+,<sup>5</sup> and absorption effects corrected with the multiscan method implemented in SADABS.<sup>6</sup> The structure was solved using the algorithm implemented in SHELXT-2014,<sup>7,8</sup> and refined by successive full-matrix least-squares cycles on  $F^2$  using the latest SHELXL-v.2014.<sup>7Error! Reference source not found.,9</sup> The non-hydrogen atoms were successfully refined using anisotropic displacement parameters. Hydrogen atoms bonded to carbon were placed at their idealized positions using the appropriate *HFIX* instructions in SHELXL and included in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacements parameters ( $U_{\text{iso}}$ ) fixed at  $1.2$  or  $1.5 \times U_{\text{eq}}$  of the relative atom.

A substantially dispersed electron density was found, most probably due to disordered solvent molecules. The attempts to unequivocally locate and model these solvent molecules revealed to be unsuccessful, and the search for the total potential solvent area using the software

package PLATON<sup>10,11</sup> confirmed the existence of cavities with potential solvent accessible void volume. Consequently, the original data set was treated with the program SQUEEZE.<sup>12</sup> The programs used for molecular graphics were MERCURY<sup>13</sup> and DIAMOND.<sup>14</sup>

Unit cell parameters and structure solution and refinement data for complex **1** are listed in Table S1. Crystallographic data for the reported structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number: CCDC-1504367. Copies of these data can be obtained free of charge via <https://summary.ccdc.cam.ac.uk/structure-summary-form>.

**Table S1. Crystallographic Data for Complex 1**

Parameter	<b>1</b>
Formula	C <sub>140</sub> H <sub>196</sub> Mn <sub>29</sub> N <sub>30</sub> O <sub>80</sub>
Fw / g mol <sup>-1</sup>	5172.52
Crystal type	Brown plate
Crystal size / mm <sup>3</sup>	0.210 × 0.090 × 0.040
Crystal system	Tetragonal
Space group	<i>P4/nnc</i>
<i>a</i> / Å	21.956(3)
<i>b</i> / Å	21.956(3)
<i>c</i> / Å	23.591(3)
<i>α</i> / °	90
<i>β</i> / °	90
<i>γ</i> / °	90
<i>V</i> / Å <sup>3</sup>	11372(3)

$Z$	2
$T / \text{K}$	150(2)
$D_c / \text{g cm}^{-3}$	1.511
$\mu / \text{mm}^{-1}$	1.627
$\theta$ range	3.696 - 25.027
Index ranges	$-25 \leq h \leq 24$
	$-26 \leq k \leq 24$
	$-25 \leq l \leq 28$
Reflections collected	90486
Independent reflections	5017 ( $R_{\text{int}} = 0.0578$ )
Data completeness	to $\theta = 25.027^\circ$ , 99.5%
Final $R$ indices $[I > 2\sigma(I)]^{a,b}$	$R1 = 0.0628$
	$wR2 = 0.1627$
Final $R$ indices (all data)	$R1 = 0.0760$
	$wR2 = 0.1712$
$(\Delta\rho)_{\text{max,min}} / \text{e \AA}^{-3}$	1.248 and $-0.755$

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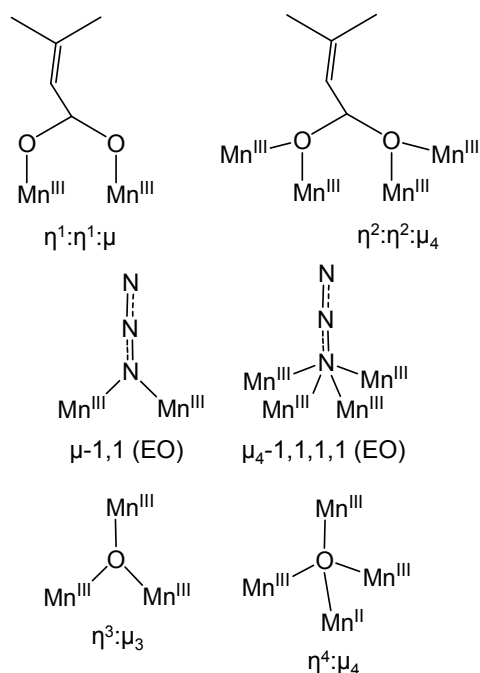
<sup>a</sup>  $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ . <sup>b</sup>  $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ ,  $w = 1/[\sigma^2(F_o^2) + [(ap)^2 + bp]$ , where  $p = [\max(F_o^2, 0) + 2F_c^2]/3$ .

**Table S2. Bond Valence Sum (BVS)<sup>a</sup> Calculations for Mn and Selected O<sup>b</sup> Atoms in Complex 1**

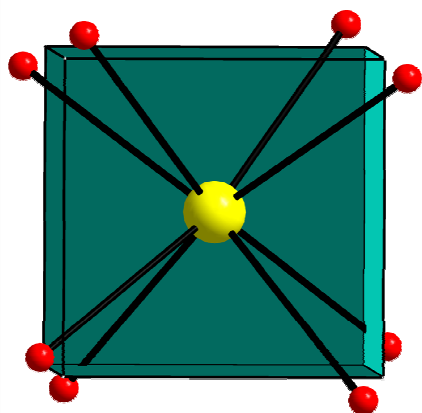
Atom	Mn <sup>II</sup>	Mn <sup>III</sup>	Mn <sup>IV</sup>
Mn1	3.22	<b>3.02</b>	3.05
Mn2	3.31	<b>3.04</b>	3.17

Mn3	3.24	<b>2.96</b>	3.11
Mn4	3.22	<b>2.96</b>	3.09
Mn5	<b>1.83</b>	1.67	1.75
BVS		Assignment	
O1	1.89	O <sup>2-</sup>	
O2	1.89	O <sup>2-</sup>	
O3	2.00	O <sup>2-</sup>	

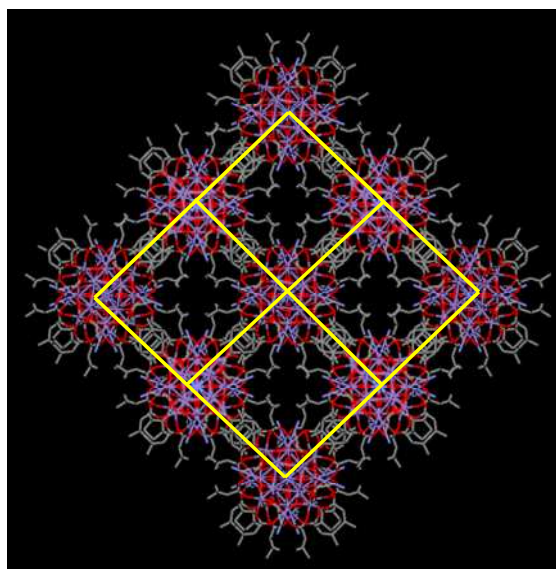
<sup>a</sup> The value in bold is the one closest to the charge for which it was calculated. The oxidation state is the nearest whole number to the value in bold. <sup>b</sup> A BVS in the ~1.8-2.0, ~1.0-1.2, and ~0.2-0.4 ranges for an O atom is indicative of non-, single- and double-protonation, respectively.



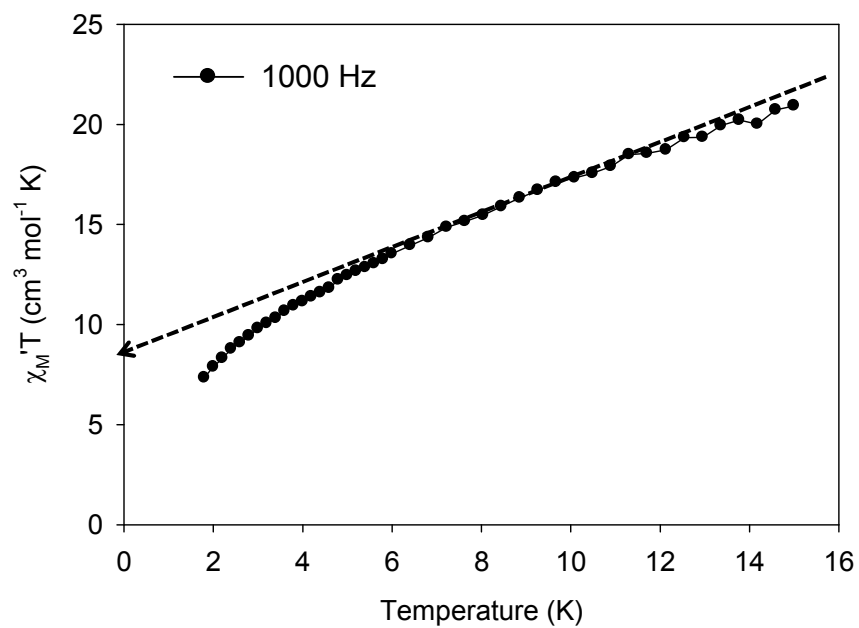
**Figure S1.** Crystallographically established coordination modes of all the ligands present in complex 1.



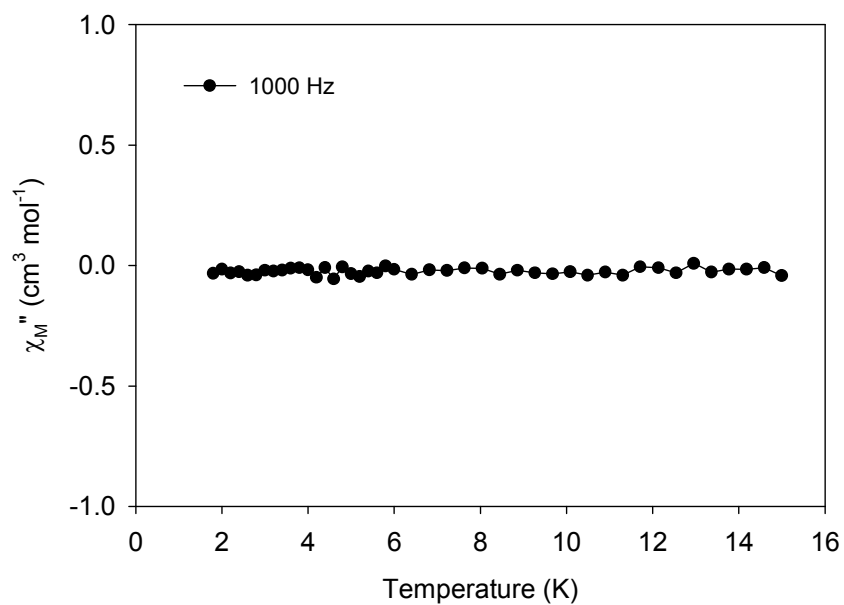
**Figure S2.** Cubic geometry of the  $\text{Mn}^{\text{II}}$  atom (Mn5) in the structure of **1**. The points connected by the black lines define the vertices of the ideal polyhedron. The so-called Continuous Shape Measures (CShM) approach essentially allows one to numerically evaluate by how much a particular structure deviates from an ideal shape. The obtained CShM value was 1.19. Values of CShM between 0.1 and 3 usually correspond to a not negligible but still small distortion from ideal geometry, while values larger than 3 refer to very distorted coordination environments.



**Figure S3.** Wireframe representation of the supramolecular grid-like structure of **1**.



**Figure S4.** The in-phase ( $\chi_M'$ ) (as  $\chi_M' T$ ) vs  $T$  ac susceptibility signal for **1** in a 3.5 G field oscillating at the indicated frequency.



**Figure S5.** The out-of-phase ( $\chi_M''$ ) vs  $T$  ac susceptibility signal for **1** in a 3.5 G field oscillating at the indicated frequency.



## References

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