Electronic Supplementary Information

A novel trigonal propeller-shaped hybrid tri-Neodymium-polyoxometalate exhibiting single-molecule magnet behavior

Hai-Long Zhang,* Xiao-Yuan Wu,* Jian-Zhen Liao,* Xiao-Fei Kuang,* Wenbin Yang,** and Can-Zhong Lu*ab

*Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P. R. China. E-mail: czlu@fjirsm.ac.cn; Fax: (+86)591-83714946; Tel: (+86)591-83705794

**Xiamen Institute of Rare-earth Materials, Haixi Institutes, Chinese Academy of Sciences, Fujian 361005, P. R. China

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1. Materials and Physical Measurements

\[(n-C_4H_9)_4N\]_2Mo_6O_{19} was synthesized according to the literature.\(^1\) All other chemicals were obtained from commercial sources and used as received without further purification. Elemental analyses (C, H, N) was carried out on Vario MICRO elemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected on Rigaku desktop MiniFlex 600 diffractometer with Cu Kα radiation (\(\lambda =1.5406\ \text{Å}\)). IR spectra were recorded in the range 4000–400 cm\(^{-1}\) on a Perkin-Elmer FT-IR spectrum 2000 spectrometer with pressed KBr pellets. Thermal analyses were performed on a TGA/DSC 1 STAR\(^\circ\) system from room temperature to 1000°C at a heating rate of 10K/min under nitrogen. The dc magnetic susceptibilities were measured with a Quantum Design MPMS-XL SQUID susceptometer under an applied magnetic field of 1 kOe in the 2-300 K range. Diamagnetic corrections were made using Pascal’s constants.\(^2\) Ac magnetic susceptibility measurements were performed on a Physical Property Measurement System (PPMS) PPMS-9 T with a 3 Oe ac oscillating field under 500 Oe dc field.

2. Experimental Section

Synthesis of \((\text{NH}_2\text{Me}_2)_2\{(\text{Nd}(\text{Mo}_4\text{O}_{13})(\text{DMF})_4)_2(\text{BTC})_2\}\_8\text{DMF} \ (\text{compound 1})\). A mixture of \((n-C_4H_9)_4\text{N}\_2\text{Mo}_6\text{O}_{19}\) (0.08 mmol, 0.109 g) and H\(_2\text{BTC}\) (0.5 mmol, 0.105 g) were dissolved in N,N-dimethylformamide (DMF) (4 mL), and 2.5 mL of an ethanol (EtOH) solution of \text{Nd(NO}_3\text{)}_3\cdot 6\text{H}_2\text{O} (0.5 mmol, 0.219 g) was added dropwise to the solution. The mixed solution was stirred at room temperature for 30 minutes to give a clear solution. The solution was sealed in a glass bottle and heated at 80 °C for 24 hours, and then slowly cooled down to the room temperature. Violet block-shaped single crystals suitable for X-ray data collection were obtained. Yield: 52% based on Mo. Elemental analysis found (calcd) for C\(_{84}\)H\(_{170}\)N\(_{23}\)O\(_{71}\)Mo\(_{12}\)Nd\(_3\), C 24.26 (23.89); H 4.21 (4.06); N 7.80 (7.63).IR (cm\(^{-1}\)) : 3418 (m), 2931 (w), 1658 (s), 1620 (m), 1562 (s), 1444 (s), 1382 (s), 1247 (s), 1114 (s), 1107 (s), 931 (s), 869 (s), 725 (m), 686 (m), 572 (m), 453 (m).

3. Crystallographic data collection and refinement

Suitable single crystal of compound 1 was mounted on a loop for the X-ray measurement. Diffraction data was collected on SuperNova (Dual source) diffractometer equipped with the CrysAlisPro X-ray crystallography data systems. The measurement was made by using graphic monochromatic Mo Kα radiation (\(\lambda = 0.71073\ \text{Å}\)) at 100 K under a cold nitrogen stream. Using Olex2,\(^3\) the structure was solved by the ShelX\(^4\) structure solution program using Intrinsic Phasing and refined with the ShelXL\(^5\) refinement package using Least Squares minimization. The crystallographic data has been deposited at the Cambridge Crystallographic Data Center with reference number CCDC 1572984. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.
4. Crystal data for compound 1

Table S1. Crystal Data and Structure Refinement Parameters for Compound 1

<table>
<thead>
<tr>
<th>Compound reference</th>
<th>Compound1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₅₄H₉₀Mo₁₂Nd₁₂O₆₃ 8(C₃H₇NO) 3(C₂H₈N)</td>
</tr>
<tr>
<td>Formula Mass</td>
<td>4222.42</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>a/Å</td>
<td>35.7841(1)</td>
</tr>
<tr>
<td>b/Å</td>
<td>18.6471(6)</td>
</tr>
<tr>
<td>c/Å</td>
<td>23.5985(7)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>120.260(3)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Unit cell volume/Å³</td>
<td>13601.1(9)</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
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<tr>
<td>No. of formula units per unit cell, Z</td>
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</tr>
<tr>
<td>No. of reflections measured</td>
<td>34634</td>
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<tr>
<td>No. of independent reflections</td>
<td>13229</td>
</tr>
<tr>
<td>Rint</td>
<td>0.0270</td>
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<tr>
<td>Final R₁ values (I &gt; 2σ(I))</td>
<td>0.0322</td>
</tr>
<tr>
<td>Final wR(F²) values (I &gt; 2σ(I))</td>
<td>0.0756</td>
</tr>
<tr>
<td>Final R₁ values (all data)</td>
<td>0.0374</td>
</tr>
<tr>
<td>Final wR(F²) values (all data)</td>
<td>0.0780</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.017</td>
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</tbody>
</table>

*R₁ = \[\frac{\sum|F_o| - |F_c|}{\sum |F_o|}\] √2.  
wR(F²) = \[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)}\]^{1/2}

Table S2. Selected bond lengths for Compound 1

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond lengths (Å)</th>
<th>Bond lengths (Å)</th>
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</thead>
<tbody>
<tr>
<td>Mo₁—O4</td>
<td>1.7492</td>
<td>Mo₃—O14</td>
</tr>
<tr>
<td>Mo₁—O5</td>
<td>2.2512</td>
<td>Mo₃—O17</td>
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<tr>
<td>Mo₁—O8</td>
<td>1.9091</td>
<td>Mo₃—O18</td>
</tr>
<tr>
<td>Mo₁—O9</td>
<td>1.7080</td>
<td>Mo₃—O19</td>
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<tr>
<td>Mo₁—O10</td>
<td>2.2245</td>
<td>Mo₃—O24</td>
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<tr>
<td>Mo₂—O3</td>
<td>1.7530</td>
<td>Mo₃—O26</td>
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<tr>
<td>Mo₂—O5</td>
<td>2.3126</td>
<td>Mo₄—O15</td>
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</table>
5. Figures of compound 1

Fig. S1 The asymmetric unit of complex 1, containing one and a half Nd centers, one and a half \{MoO$_{13}$\} POMs, a deprotonated BTC ligand, six coordinated DMF molecules, one and a half (NH$_2$Me$_2$)$^+$ cations and four uncoordinated DMF molecules (omitted for clarity). Nd (green), O (red), C (gray), N (blue), Mo (dark teal), H (light gray).
**Fig. S2** The 2D hydrogen-bonded layer in 1. Nd (green), MoO$_6$ octahedral (orange), O (red), C (gray), N (blue), H (light gray).

**Fig. S3** The 3D packing view of 1 along the b axis. Nd (green), MoO$_6$ octahedral (orange), O (red), C (gray), N (blue), H (light gray).
6. Magnetic data

**Fig. S4** Temperature dependence of in-phase ac susceptibility at different ac frequency under a 500 Oe dc field for 1 (the solid lines are for eye guide).

**Fig. S5** Frequency dependence of the in-phase ac susceptibility from 2.0 to 6.0 K under a 500 Oe dc field for 1 (the solid lines are the best fitting of experimental data the generalized Debye model).

**Fig. S6** Cole–Cole plots at different temperatures (3.0 – 5.0 K) for 1 (the solid lines are the best fitting of experimental data to a generalized Debye model).
Table S3 Selected parameters obtained by fitting out-of-phase ac magnetic susceptibility ($\chi''$) vs frequency (ν) plots of 1 using Debye model.

<table>
<thead>
<tr>
<th>T/K</th>
<th>τ/ms</th>
<th>α</th>
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<tbody>
<tr>
<td>4.0</td>
<td>0.1075</td>
<td>0.07</td>
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<tr>
<td>4.5</td>
<td>0.0583</td>
<td>0.03</td>
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<tr>
<td>5.0</td>
<td>0.0297</td>
<td>0.04</td>
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<tr>
<td>5.5</td>
<td>0.0168</td>
<td>0.05</td>
</tr>
<tr>
<td>6.0</td>
<td>0.0125</td>
<td>0.04</td>
</tr>
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</table>

Fig. S7 Magnetization measurements vs applied field plot for 1 at 2.0 K.

7. Thermogravimetric analyses

Fig. S8 The TGA curve of complex 1.
8. X-ray Powder Diffraction

Fig. S9 A comparison of PXRD patterns between the as-synthesized bulk material of 1 and the simulated one from the single crystal diffraction data of 1.

9. IR spectrum

Fig. S10 The IR spectrum of compound 1.

10. Hydrolysis mechanism of DMF and the formation of dimethylamine cations

\[ \text{H}_{2}\text{O} + \text{HCOOH} + \text{NH}_2\text{(CH}_3\text{)}_2 \rightarrow (\text{CH}_3\text{)}_2\text{NH}_2 + \text{H}^+ \]
H$_2$O sources: Nd(NO$_3$)$_3$·6H$_2$O and impurity of DMF and EtOH (there are always a very little amount of water in DMF and EtOH)
H$^+$ sources: H$_3$BTC

11. References