Supplementary Information

Two-dimensional frameworks built from Single-Molecule Magnets

Athanassios D. Katsenis, Ross Inglis, Alessandro Prescimone, Euan K. Brechin, and Giannis S. Papaefstathiou

gspapaef@chem.uoa.gr
Laboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, 157 71 Zografou, Greece. Fax: +30 210 – 727 – 4782; Tel: +30 210 –727 –4840; E-mail:
ebrechin@staffmail.ed.ac.uk
EaStCHEM School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK. Fax: +44 111 – 275 – 4598; Tel.: +44 131 650 7545; E-mail:

Experimental details

Complex 1: Mn(ClO$_4$)$_2$∙6H$_2$O (0.330g, 0.900mmol) and saoH$_2$ (0.122g, 0.900mmol) were dissolved in MeOH (20mL). MeONa (1.000mmol) was then added under stirring (solution A) and the solution stirred for another 40 min. A methanolic solution (10mL) containing tmaH$_3$ (0.025g, 0.100mmol) was then added to solution A and the solution stirred for about 1 min. The resulting solution left undisturbed. X-ray quality, dark green, crystals of 1 were obtained in 40% yield. Elemental analysis for 1: Calculated (%) for C$_{55}$H$_{51}$O$_{24}$N$_6$Mn$_6$ (vacuum dried complex 1): C: 43.63; H: 3.60; N: 5.53; Found: C: 43.58; H: 3.55; N: 5.59.

Complex 2: To a methanolic solution of Mn(ClO$_4$)$_2$∙6H$_2$O (0.330g, 0.900mmol), saoH$_2$ (0.122g, 0.900mmol) and tmaH$_3$ (0.025g, 0.100mmol), MeONa (1.000mmol) was added in small portions under stirring to form a dark green slurry solution. The solution turns to clear dark green after a stirring period of 14 mins. The resulting solution left undisturbed to form dark green crystals of 2 in 40% yield. Elemental analysis for 2: Calculated (%) for C$_{51.32}$H$_{51.25}$O$_{22.67}$N$_6$Mn$_6$ (vacuum dried complex 2): C: 42.78; H: 3.36; N: 5.83; Found: C: 42.72; H: 3.28; N: 5.90.
**Fig. S1** Plot of $\chi_M T$ versus $T$ for complexes **1** and **2**. The data could not be successfully fitted because each complex has more than one crystallographically independent $[\text{Mn}_6]$ in the crystal. For comparison the data for $[\text{Mn}_6]$ with similar torsion angles, reference 3c, are also plotted as **3** and **4**.

**Fig. S2** Plot of magnetisation ($M/N\mu_B$) versus field ($H$) at 2 K for **1** and **2**. The data for each could not be successfully fitted using a simple model that assumes only population of the ground state. The reason, as with most members of this family, is the presence of multiple low-lying excited states and the existence of more than one crystallographically independent $[\text{Mn}_6]$ in the crystal.
Fig. S3  Plot of $\chi_M T$ versus $T$ for complex 1 at the indicated temperature and frequency ranges.

Fig. S4  Plot of $\chi_M T$ versus $T$ for complex 2 at the indicated temperature and frequency ranges.
**Fig. S5** Plot of $\chi_{\alpha''}$ versus $T$ for complex 2 at the indicated temperature and frequency ranges. Inset: Arrhenius plots constructed from the $\chi''$ data to afford $\tau_0 = 5.6 \times 10^{-8}$ s and $U_{eff} \approx 24$ K.

**Fig. S6** The IR spectra (KBr disks) of complex 1 (left) and 2 (right) in the 4000 – 400 cm$^{-1}$ region.
Table S1: Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for 1.

<table>
<thead>
<tr>
<th>D'-H···A</th>
<th>D···A</th>
<th>H··A</th>
<th>&lt;D'H·A</th>
<th>D' = donor atom. A = acceptor atom.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O32K-H32K···O1N [3-x,3-y,-z]</td>
<td>2.698(7)</td>
<td>1.88(1)</td>
<td>164(1)</td>
<td></td>
</tr>
<tr>
<td>O1W-H1W···O33K [3-x,3-y,-z]</td>
<td>2.694(7)</td>
<td>1.86(1)</td>
<td>176(1)</td>
<td></td>
</tr>
<tr>
<td>O53D-H53D···O1B [1-x,2-y,1-z]</td>
<td>2.660(7)</td>
<td>1.84(1)</td>
<td>163(1)</td>
<td></td>
</tr>
<tr>
<td>O1Q-H1Q···O</td>
<td>2.773(7)</td>
<td>1.94(1)</td>
<td>169(1)</td>
<td></td>
</tr>
</tbody>
</table>