Electronic Supplementary Information

Linking magnetic $\text{M}^{\text{II}}$–[M$^{\text{V}}$(CN)$_8$] chains into 2D inorganic–organic hybrid materials

O. Stefańczyk,* a,b,c A. M. Majcher,d M. Rams,d W. Nitek,a C. Mathonière,b,c and B. Sieklucka*a

a Faculty of Chemistry, Jagiellonian University in Kraków, Ingardena 3, 30–060 Kraków, Poland.
b CNRS, ICMCB, UPR 9048, F–33600 Pessac, France.
c Univ. Bordeaux, ICMCB, UPR 9048, F–33600 Pessac, France.
d Institute of Physics, Jagiellonian University in Kraków, Łojasiewicza 11, 30–348 Kraków, Poland.

Contents

Table S1. Results of continuous shape measures analysis for M$^{\text{V}}$ centers.
Table S2. Results of continuous shape measures analysis for M$^{\text{II}}$ centers.
Figure S1. IR spectra in full range, in the ν(C≡N) region and in the fingerprint region for 1 - 3.
Figure S2. ORTEP diagrams of asymmetric units of 2 and 3 with selected atoms labeling. Superimposed structural diagrams for 1 – 3.
Figure S3. Local environments of the metal centers of 1 and other Co$^{\text{II}}$–W$^{\text{V}}$ systems.
Figure S4. Local environments of the metal centers of 2, 3 and another Cu$^{\text{II}}$–M$^{\text{V}}$ system.
Figure S5. Crystal packing for 1 – 3 and other systems containing 3,2–chain entities.
Figure S6. The $\chi_{\text{M}}(f)$ and $\chi_{\text{M}}''(f)$ curves for 1 as a function of the AC frequency measured in $H_{\text{dc}} = 0, 0.5$ and 1 kOe ($H_{\text{ac}} = 1$ Oe) at $T = 1.8$ K.
Figure S7. The first derivative of magnetization vs. magnetic field plots for 1 – 3.
Table S1. Results of continuous shape measures analysis for M^V centers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Geometry</th>
<th>S_{BTP}</th>
<th>S_{SAPR}</th>
<th>S_{TDD}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ideal BTP–8</td>
<td>0.000</td>
<td>2.262</td>
<td>2.709</td>
</tr>
<tr>
<td></td>
<td>ideal SAPR–8</td>
<td>2.262</td>
<td>0.000</td>
<td>2.848</td>
</tr>
<tr>
<td></td>
<td>ideal TDD–8</td>
<td>2.709</td>
<td>2.848</td>
<td>0.000</td>
</tr>
<tr>
<td>1</td>
<td>[W(CN)_8]</td>
<td>2.064</td>
<td>2.275</td>
<td>0.345</td>
</tr>
<tr>
<td>2</td>
<td>[W(CN)_8]</td>
<td>1.954</td>
<td>1.774</td>
<td>0.393</td>
</tr>
<tr>
<td>3</td>
<td>[Mo(CN)_8]</td>
<td>1.966</td>
<td>1.674</td>
<td>0.497</td>
</tr>
</tbody>
</table>

S_{BTP} – the shape measure relative to the bicapped trigonal prism; S_{SAPR} – the shape measure relative to the square antiprism; S_{TDD} – the shape measure relative to the triangular dodecahedron; smaller S–value reflect a better match with the ideal geometry (S = 0).

Table S2. Results of continuous shape measures analysis for M^II centers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Geometry</th>
<th>S_{OC}</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC–6</td>
<td></td>
<td>0.000</td>
</tr>
<tr>
<td>1</td>
<td>[Co(NC)_4(DMF)_4]</td>
<td>0.040</td>
</tr>
<tr>
<td>1</td>
<td>[Co(NC)_4(pyz)(DMF)_3]</td>
<td>0.345</td>
</tr>
<tr>
<td>2</td>
<td>[Cu(NC)_4(DMF)_4]</td>
<td>0.185</td>
</tr>
<tr>
<td>2</td>
<td>[Cu(NC)_4(pyz)(DMF)_3]</td>
<td>0.831</td>
</tr>
<tr>
<td>3</td>
<td>[Cu(NC)_4(DMF)_4]</td>
<td>0.426</td>
</tr>
<tr>
<td>3</td>
<td>[Cu(NC)_4(pyz)(DMF)_3]</td>
<td>0.843</td>
</tr>
</tbody>
</table>

S_{OC} – the shape measure relative to the octahedron; smaller S–value reflect a better match with the ideal geometry (S = 0).
Figure S1. IR spectra in full range (4000 - 550 cm\(^{-1}\)) (a), in the \(\nu(C≡N)\) region (2250 - 2000 cm\(^{-1}\)) (b) and in the fingerprint region (1800 - 550 cm\(^{-1}\)) (c) for 1 (blue), 2 (black) and 3 (red).
Figure S2. ORTEP diagrams of asymmetric units of 2 (a) and 3 (b) with selected atoms labeling. Colors used: C – gray, Co – yellow, Cu – orange, N – blue, Mo – green, O – red, W – purple. Thermal ellipsoids of 50% probability are shown. c) Superimposed structural diagrams for 1 (blue), 2 (black) and 3 (red).
Figure S3. Local environments of the metal centers of 1 and other Co$^{II}$–W$^{V}$ systems.
Figure S4. Local environments of the metal centers of 2, 3 and another CuII-MV system.
**Figure S5.** Crystal packing for 1–3 and other systems containing 3,2–chain entities.

**Figure S6.** The $\chi_M'(f)$ (full symbols) and $\chi_M''(f)$ curves (open symbols) for 1 as a function of the AC frequency measured in $H_{dc} = 0$ (black), 0.5 (red) and 1 kOe (blue) ($H_{dc} = 1$ Oe) at $T = 1.8$ K.
Figure S7. The first derivative of magnetization vs. magnetic field plots for 1 (blue), 2 (black) and 3 (red).