Supporting Information

Directed synthesis of \{\text{Cu}^{II}\text{Zn}^{II}\}_2\} and \{\text{Cu}^{II}\text{Zn}^{II}\}_8\} heterometallic complexes

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Figure S1. ESI\(^+\) mass spectra for 1 (right) and 2 (left).

The majority of the peaks have been assigned considering the molecular weight and charge of the potential cations which could be present following fragmentation, and according to the tendency of \(H_6L\) to display a certain arrangement around the different metal ions. Both spectra for complexes 1 and 2 show common peaks related to a metallo-organic monomeric species ([Cu(H\(_5\)L)]\(^+\)) and other polynuclear complex cations containing various Cu(II) and/or Zn(II) ions ([Cu\(_2\)(H\(_4\)L)(H\(_5\)L)]\(^+\), [Cu\(_2\)(H\(_3\)L)(H\(_4\)L)Zn]\(^+\), [ClCu\(_2\)(H\(_4\)L)\(_2\)Zn]\(^+\)). Taking into account the fragmentation observed in both spectra, the central chloride in 2 could act as template to form the \{Cu\(_8\)Zn\(_8\)\} ring, although assignment of the species is complicated by the presence of overlapping peaks. For 2, the peaks observed in the region of m/z = 800-900 suggest a possible rearrangement of the \{Cu\(_6\)Zn\(_6\)\} units to form a larger Cu(II)/Zn(II) complex.
Figure S2. Overlay of the inequivalent molecules in the asymmetric unit of 1.

Figure S3. Intramolecular hydrogen bonding interactions in complex 2. The hydrogen bonds between the central Cl···H(OH) are shown as dashed black lines. C, grey; Cl, green; Cu, turquoise; hydroxyl H atoms highlighted in dark green; N, blue; O, red; Zn, lavender.
Figure S4. Intramolecular hydrogen bonding interactions in complex 2. The hydrogen bonds between O(OH)···H(H₄L²⁻) are shown as dashed black lines. C, grey; Cl, green; Cu, turquoise; hydroxyl H atoms highlighted in black; N, blue; O, red; Zn, lavender.
Figure S5. Molar magnetic susceptibility ($\chi_M$) vs. temperature ($T$) of 1 (left) and 2 (right) in an applied field of 10000 (1) and 5000 (2) Oe. The black lines correspond to the fit.

Equation S1

$$H = -2J \sum_i s_i \cdot s_j + g\mu_B H \sum_i s_i$$

Equation S2

$$H = -2J \left[ \sum_i s_i \cdot s_{i+1} + \sum_i s_i \cdot s_1 \right] + g\mu_B \sum_i s_i$$

Spin Hamiltonians used to fit the magnetic data for complexes 1 and 2, respectively, with a single parameter $J$ describing the exchange interaction between Cu(II) centres ($\vec{s}$ denotes the spin operator). The second term is the Zeeman interaction, with $g$ the isotropic single-ion $g$ factor, $\mu_B$ the Bohr magneton and $H$ the magnetic field.

The sharp increase of the $\chi_M$ value at low temperatures in the $\chi_M$ vs. $T$ plot for 1 indicates the presence of a small paramagnetic impurity commonly observed in this kind of system, and is in accord with the value obtained from the fit.$^{1,2}$
Figure S6  X-band EPR spectrum of 1 recorded in MeOH solution at 293 K (experimental conditions: frequency, 9.4269 GHz; power, 20 mW; modulation, 0.3 mT). Experimental data are represented by the black line; simulation is depicted by the red trace.

\[ g_{\text{iso}} = 2.109 \]

\[ A_{\text{iso}^{63,65}\text{Cu}} = 69 \times 10^{-4} \text{ cm}^{-1} \]

Although complex 1 appears to decompose in MeOH, we assume that the \( g_{\text{iso}} \) value of the resultant Cu bis-tris propane monomeric unit should be approximately the same as the \( g_{\text{iso}} \) value for 1.

Table S1. Selected structural parameters and coordination environments of complexes 1, 2 and \{Cu₂Zn₂(DEA)₄\}.

<table>
<thead>
<tr>
<th>Complex</th>
<th>1</th>
<th>2</th>
<th>{Cu₂Zn₂(DEA)₄}³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry of Cu(II)</td>
<td>( C_{4v} )</td>
<td>( D_{4h} )</td>
<td>( D_{4h} )</td>
</tr>
<tr>
<td>( d_{(\text{Cu} \cdots \text{Cu})} ) (Å)</td>
<td>5.724(3)</td>
<td>5.685(2)</td>
<td>5.706(9)</td>
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<tr>
<td>( d_{(\text{Cu} \cdots \text{Zn})} ) (Å)</td>
<td>3.434(4)</td>
<td>3.389(2)</td>
<td>3.435(7)</td>
</tr>
<tr>
<td>( \alpha_{(\text{Cu} \cdots \text{Zn} \cdots \text{Cu})} ) (°)</td>
<td>115</td>
<td>88.6</td>
<td>112.4</td>
</tr>
<tr>
<td>( \beta_{(\text{Cu}OZn)} ) (°)</td>
<td>124.58(7)</td>
<td>122.52(4)</td>
<td>123.69(1)</td>
</tr>
</tbody>
</table>
Figure S7. Detail of the crystal structure of 2. Cu, turquoise; O, red; Zn, lavender.
References