

SUPPORTING INFORMATION

An original 3D coordination polymer constructed from trinuclear nodes and tetracarboxylato spacers

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Synthesis

All solvents were analytical grade and used as received. 1,2,4,5-Benzenetetracarboxylic acid (H₄btec), Cu(ClO₄)₂·6H₂O and triethyl amine (NEt₃) were purchased from commercial sources and used as received. 2,4,6-Triformylphloroglucinol¹ and the corresponding trinucleating Schiff base ligand (H₃felden) were prepared using the reported procedures.² **Caution!** *Although no problems were encountered, perchlorate salts are potentially explosive, thus they should be handled with care and prepared in small quantities.*

Synthesis of $\infty_3[\{\text{Cu}_3(\text{felden})\}_4(\text{btec})_3] \cdot 17\text{H}_2\text{O}$ **1**

To a solution of H₃felden (0.042 mmol, 18 mg) in a mixture of DMF/MeOH/H₂O (2:1:1, 5 mL) deprotonated with triethylamine (35 μ L) was added Cu(ClO₄)₂·6H₂O (0.09 mmol, 33 mg) dissolved in the above mentioned solvent mixture (5mL). The resulting solution was left to slowly diffuse through a MeOH/DMF layer (2:1, 5 mL) into 10 mL MeOH of 1,2,4,5-benzenetetracarboxylic acid (0.055 mmol, 14 mg) deprotonated with NEt₃ (20 μ L). Green single crystals suitable for X-ray measurements appeared within one month. Yield (based on H₃felden): 16 mg, 30 %. Selected IR data (KBr, cm⁻¹): 3335 (m), 3211 (w), 2896 (w), 2870 (w), 1624 (s), 1603 (s), 1469 (s), 771 (s).

Physical measurements

The **IR spectra** (KBr pellets) were collected on a Bruker Tensor 37 spectrophotometer in the 4000–400 cm⁻¹ range.

Specific surface area and pore size distribution was determined through BET method using N₂ adsorption-desorption analysis on Autosorb IQ (Quantachrome, USA) analyser. The samples were degassed at 25 °C for 240 min. Increased of the degassing temperature (50 and 80 °C) caused decomposing of the samples. The specific surface area was calculated by using the Brunauer–Emmett–Teller (BET) equation through linearity criterion in the P/P_0 range of 0.1 – 0.3. The textural properties were completed by investigating the pore size distribution using the Barrett–Joyner–Halenda (BJH) equation. The values of the obtained pore volume and BET surface are 0.019 cm³/g and 35.066 m²/g, respectively. This low experimental value of the BET surface area can be the result of the collapsing of the crystalline structure by solvent removal.

Thermogravimetry was performed using a Shimadzu DTG - 60 instrument under dry nitrogen flow (50 mL/min); temperature range was 25–800 °C with a heating-up rate of 5 °C/min, with platinum crucible as sample holder.

The **magnetic measurements** were performed on a freshly prepared sample with a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. The magnetic data were corrected for the diamagnetic contributions of the constituent atoms as well as for the sample

holder (a plastic bag). A value of $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ was used for the temperature independent paramagnetism of each copper(II) ion.

Crystal structure

X-ray diffraction data for **1** was obtained at the XRD2 structural biology beamline, Sincrotrone Elettra Trieste, Italy. The beamline is equipped with Arinax MD2S high-throughput diffractometer coupled with Pilatus 6M area detector and open flow nitrogen cryostat and cryogenic sample changer. A superconducting wiggler acts as the beamline light source and the X-ray wavelength is selected using a cryogenically cooled dual-crystal Si(111) monochromator. A total of 13 crystals from 3 distinct crystallization experiments were tested in order to ensure reproducibility and sample purity. Data collections were performed at 100 K using an X-ray wavelength of 0.70000 Å and consisted of a simple 360 omega scan. Indexation and frame integration were performed using the XDS package³ and space group assignment was further confirmed using Pointless from the CCP4 suite.⁴ All samples showed relatively poor resolution, generally above 1 Å. The structure of **1** was solved using the data from the best crystal, with a 0.9 Å resolution. The structure was solved using intrinsic phasing methods of SHELXT and refined by full-matrix least-squares minimization on F² with SHELXL^{5,6} within the graphical interface of Olex2.⁷ Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in calculated positions and refined using riding model. As turned out, all the atoms in the asymmetric unit are disordered over two close positions with site occupancy of 0.5 and their positional parameters were refined in combination with PART and SADI restraints with equivalent displacement parameters for paired components. All tested crystals exhibit low diffraction capacity and the resolution of the collected X-ray data has been estimated to be 0.90 Å. Consequently, the model of the structure was refined with anisotropic temperature factors for all atoms. The total solvent accessible volume was calculated with Mask routine available in Olex2 program using the probe radii of 1.2 Å and a resolution of 0.2 Å.

Crystal data, data collection parameters and structure refinement details are given in Table S1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC: 2044634.

Table S1. Crystallographic data, details of data collection and structure refinement parameters for **1**

Empirical formula	C ₁₁₄ H ₁₃₅ Cu ₁₂ N ₂₄ O ₃₆
<i>M</i> (g mol ⁻¹)	3179.93
Temperature, (K)	293(2)
Wavelength, (Å)	0.700
Crystal system	<i>cubic</i>
Space group	<i>I</i> 23 no. 197
<i>a</i> (Å)	36.336(4)
<i>b</i> (Å)	36.336(4)
<i>c</i> (Å)	36.336(4)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	47975(17)
<i>Z</i>	8
<i>D</i> _c (g cm ⁻³)	0.881
μ (mm ⁻¹)	1.045
Reflections collected	219765
Independent reflections	11372 [<i>R</i> _{int} = 0.0475]
Goodness-of-fit on <i>F</i> ²	1.028
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0696, 0.2009
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0777, 0.2162
Largest diff. peak and hole (eÅ ⁻³)	0.736, -0.521

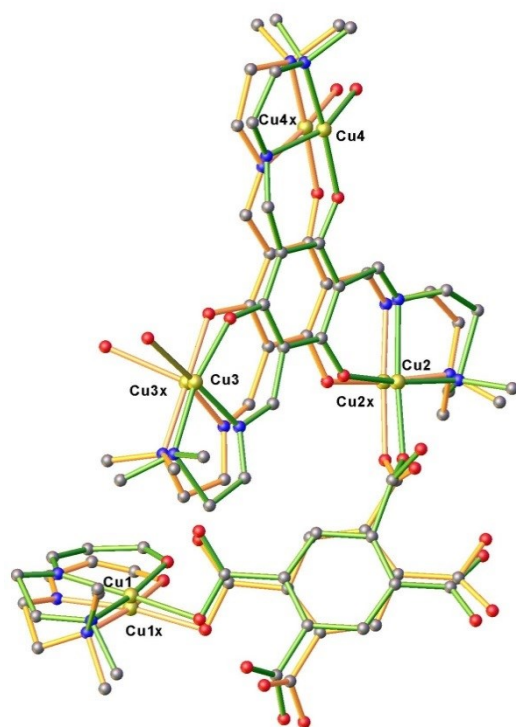


Figure S1. Perspective view of the asymmetric unit showing the disorder of the atoms.
(symmetry operations: $i = 0.5-z, 0.5+x, 0.5-y$; $ii = -0.5-y, 0.5-z, 1.5+x$)

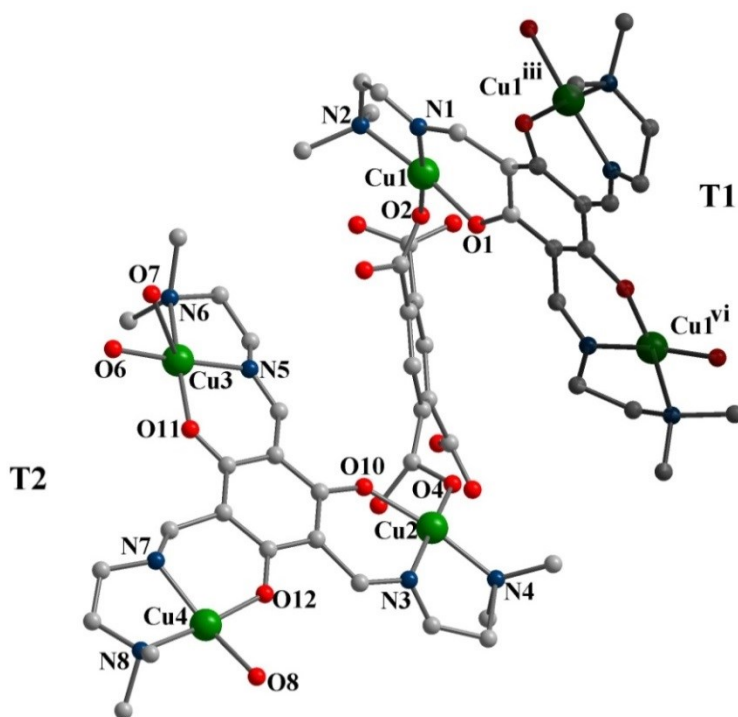


Figure S2. Detail of the crystal structure of **1** showing the two different type of triangles (T1 and T2) formed by the trinuclear nodes linked through the tetracarboxylato spacer. (Symmetry operations: $^{iii} = y, -1+z, 1+x$, $^{vi} = -1+z, x, 1+y$).

Table S2. Selected bond distances (Å) and angles (°).

<i>Bond lengths (Å)</i>	<i>Angles (°)</i>	
Cu1 - O1 = 1.914(8)	O2 - Cu1 - N2 = 91.4(8)	O6 ⁱⁱ - Cu3 - N5 = 174.5(7)
Cu1 - O2 = 1.961(18)	N2 - Cu1 - N1 = 82.5(7)	N6 - Cu3 - O11 = 168.3(7)
Cu1 - N1 = 1.982(9)	N1 - Cu1 - O1 = 95.3(6)	O12 - Cu4 - N7 = 95.5(5)
Cu1 - N2 = 1.990(9)	O1 - Cu1 - O2 = 90.7(6)	N7 - Cu4 - N8 = 79.4(6)
Cu2 - O4 = 1.934(9)	O2 - Cu1 - N1 = 173.8(7)	N8 - Cu4 - O8 ⁱ = 92.4(7)
Cu2 - O10 = 1.921(9)	O1 - Cu1 - N2 = 172.3(6)	O8 ⁱ - Cu4 - O12 = 92.4(6)
Cu2 - N3 = 2.050(19)	O10 - Cu2 - N3 = 88.4(6)	O12 - Cu4 - N8 = 175.0(7)
Cu2 - N4 = 1.986(9)	N3 - Cu2 - N4 = 85.9(7)	O8 ⁱ - Cu4 - N7 = 157.0(7)
Cu3 - O11 = 1.926(8)	N4 - Cu2 - O4 = 92.1(7)	
Cu3 - N5 = 1.958(9)	O4 - Cu2 - O10 = 93.1(6)	
Cu3 - N6 = 1.999(9)	O10 - Cu2 - N4 = 172.2(7)	
Cu3 - O6 ⁱⁱ = 1.880(16)	N3 - Cu2 - O4 = 174.9(6)	
Cu4 - O12 = 1.923(8)	O6 ⁱⁱ - Cu3 - O11 = 89.0(7)	
Cu4 - O8 ⁱ = 1.964(14)	O11 - Cu3 - N5 = 90.5(5)	
Cu4 - N7 = 1.957(9)	N5 - Cu3 - N6 = 81.8(6)	
Cu4 - N8 = 1.982(9)	N6 - Cu3 - O6 ⁱⁱ = 99.5(7)	
<i>i</i> = 0.5-z, 0.5+x, 0.5-y		
<i>ii</i> = -0.5-y, 0.5-z, 1.5+x		

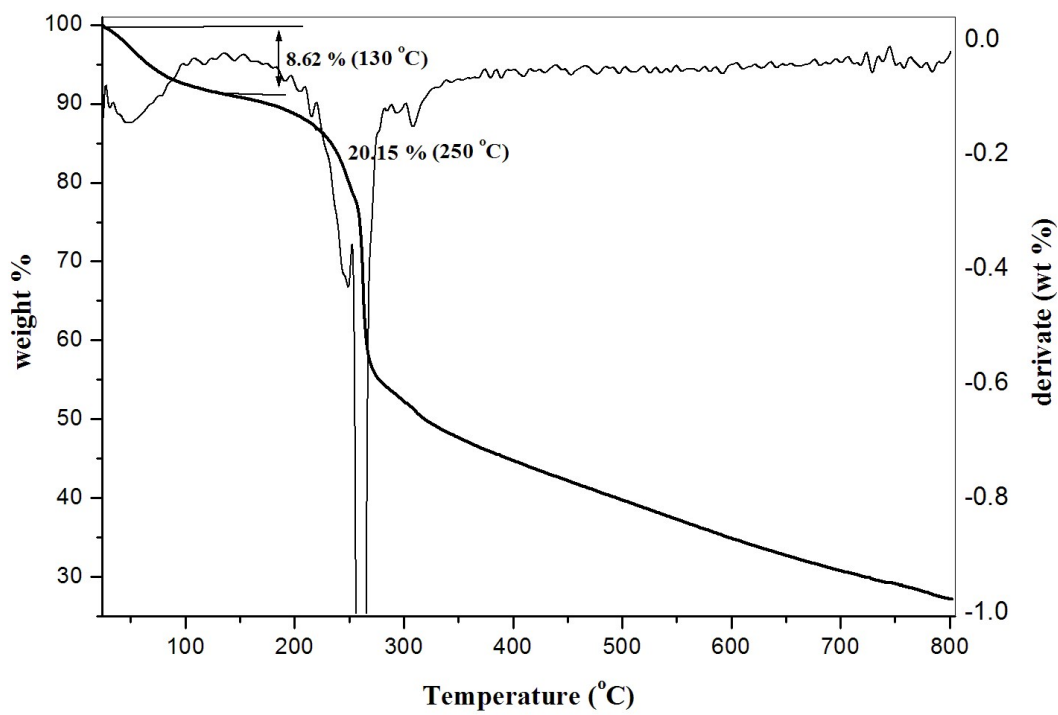


Figure S3. Thermogravimetric data for $\infty_3[\{\text{Cu}_3(\text{felden})\}_4(\text{btec})_3] \cdot 17\text{H}_2\text{O}$ **1**.

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