# An unusual zig-zag 1D copper(II) coordination polymer displaying magnetic phase transition

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## Synthesis section

A mixture of $H_2L$ (0.05 mmol, 0.019 g), Him (0.011 g, 0.1 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.15 mmol, 0.03 g) and 6ml of acetonitrile/$H_2O$ (v/v=1:1) was stirred for 30 min and then transferred and sealed in a 25-mL Teflon-lined reactor and heated to 120 °C for 72 h, and then cooled to room temperature at a rate of 2 °C/h. Blue block crystals of **1** were obtained in 51 % yield based on copper. Anal. (%) calcd for $C_{28}H_{24}CuN_4O_6$: C, 58.38 %; H, 4.20 %; N, 9.73 %; found: C, 58.01 %; H, 4.12%; N, 9.55 %. IR: 3410(m); 2941(m); 1604(v); 1498(vs); 1359(m); 1246(v); 1159(vs); 1046(m); 1002(m); 839(m); 777(m); 751(m); 663(vs).

*X-ray Crystallography*

Single crystal X-ray diffraction data collection were carried out on a Bruker SMART APEX diffractometer that was equipped with a graphite monochromated MoKα radiation (λ = 0.71073 Å) by using an ω-scan technique. The intensities of the absorption effects were corrected by using SADABS. The structures were solved by direct methods (SHLEXS-2014) and refined by a full-matrix least-squares procedure based on $F^2$ (Shelxl-2014). The space group is not *C*2/c. Although weak, the h0l = 2n+1 reflections are not systematically absent, so that the space group would be either *C*2 or *C*2/m only. Refinement in *C*2 gave a satisfactory model when the model was treated as an inversion twin. The twinning is nearly 1:1. The Cu1 and Cu2 atoms are disordered with respect to each other; the occupancies refined to an approximate 2:1 ratio. Owing to the different occupancies of the Cu atoms, the occupancies of the hydrogen atoms were appropriately set to those coordinated Cu atoms. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic details and selected bond dimensions for **1** are listed in Tables S1 and S2. CCDC: 1565811.

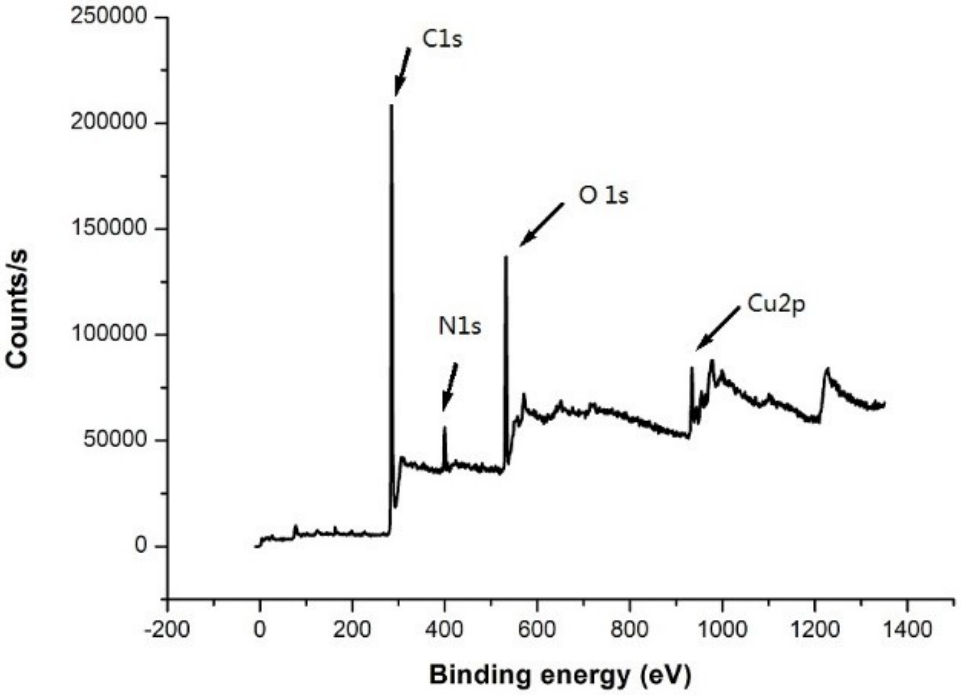


Fig. S1 XPS for the title compound.

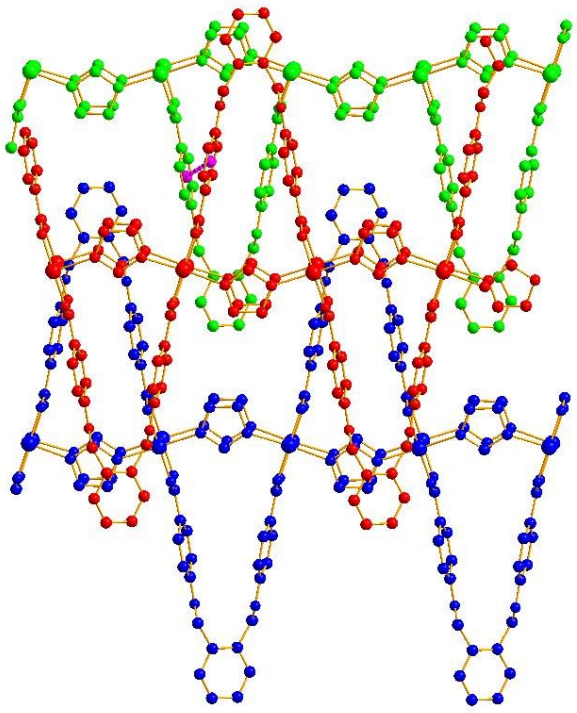

Fig. S2 view of the packing model between adjacent 1D chains.

**Thermal Properties**

In order to examine the thermal stability of **1**, thermal gravimetric analysis (TGA)were carried out for 1 between 25 and 1000 °C under nitrogen atmosphere at the heating rate of 10 °C $min^{-1}$, as shown in Fig.S3. The TGA curve of **1** showed the crystal can keep stable until 240 °C with a sharp weight loss occuring in the temperature range of 245–720 °C for degradation of organic ligands L and Him (82.5 5%, calculated value of 87.30 %). The remaining weight corresponds to formation of CuO. Decompositions of this type have previously been observed for similar Cu(II)-based CPs.

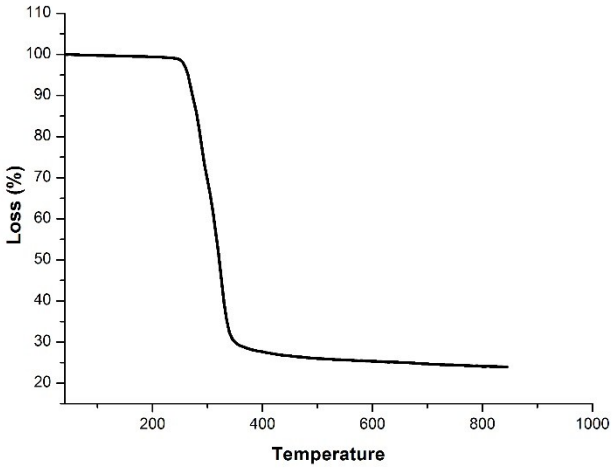


Fig. S3 view of TGA plots in **1**.

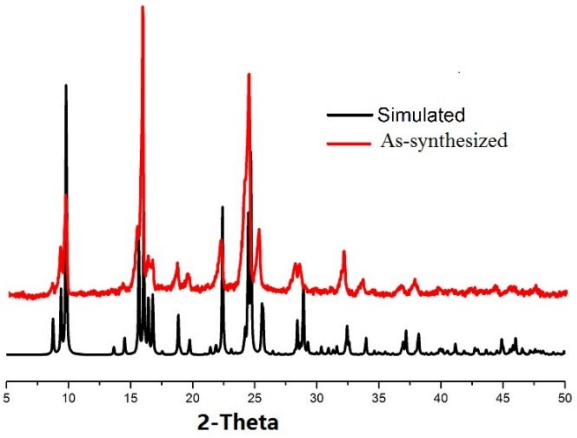


Fig. S4 view of the PXRD in **1**.

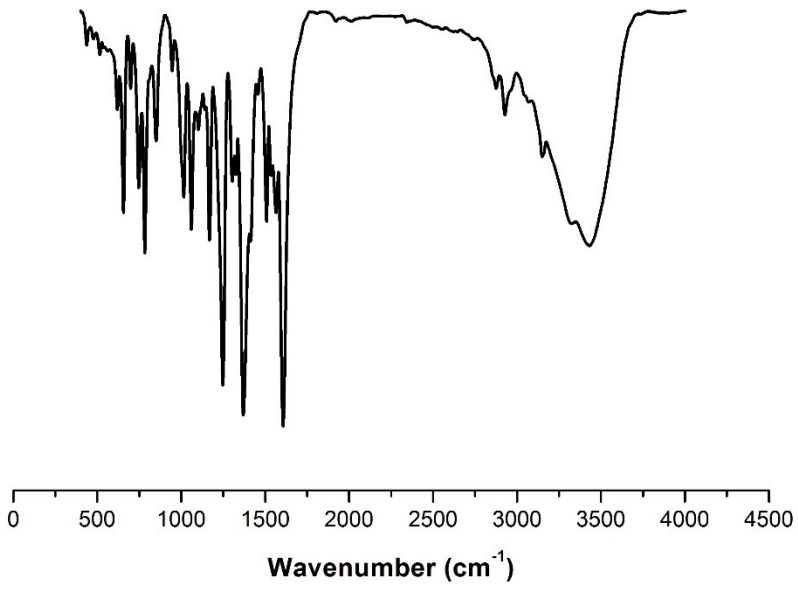


Fig. S5 view of IR in **1**.

**Table S1. Crystallographic data and structure refinement details for 1**

| Parameter | **1** |
|---|---|
| Formula weight | 576.05 |
| Crystal system | Monoclinic |
| Space group | *C2* |
| Crystal color | Blue |
| *a*, Å | 14.8222(12) |
| *b*, Å | 18.034(2) |
| *c*, Å | 11.3463(12) |
| *α*, ° | 90 |
| *β*, ° | 124.6350(10) |
| *γ*, ° | 90 |
| *V*, Å $^3$ | 2495.4(4) |
| *Z* | 4 |
| $\rho_{calcd}$, g/cm$^3$ | 1.533 |

| | |
|---|---|
| μ, $mm^{-1}$ | 0.928 |
| $F$(000) | 1188 |
| θ Range, deg | 3.1-27.5 |
| Reflection collected | 5548 |
| Independent reflections ($R_{int}$) | 0.033 |
| Reflections with $I > 2\sigma(I)$ | 4467 |
| Number of parameters | 339 |
| $R_1$, $wR_2$ ($I > 2\sigma(I)$)* | 0.0463, 0.1132 |
| $R_1$, $wR_2$ (all data)** | 0.0617, 0.1217 |

* $R = \sum(F_o - F_c)/\sum(F_o)$, ** $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2\}^{1/2}$.

**Table S2.** Selected bond distances (Å) and angles (deg) for **1**

| | | | |
|---|---|---|---|
| | | **1** | |
| Cu(1)-O(1) | 1.884(6) | Cu(1)-N(1) | 2.086(6) |
| Cu(1)-O(4) | 1.864(4) | Cu(1)-N(3) | 2.087(6) |
| Cu(2)-O(2) | 1.846(5) | Cu(2)-O(5) | 1.817(7) |

| | | | |
|---|---|---|---|
| | | **1** | |
| O(1)-Cu(1)-O(4) | 164.9(3) | O(1)-Cu(1)-N(1) | 91.2(2) |
| O(1)-Cu(1)-N(3) | 91.6(2) | O(4)-Cu(1)-N(1) | 90.2(2) |
| O(4)-Cu(1)-N(3) | 90.6(2) | N(1)-Cu(1)-N(3) | 166.3(2) |
| O(2)-Cu(2)-O(5) | 155.3(3) | O(2)-Cu(2)-N(2)#1 | 89.8(3) |
| O(2)-Cu(2)-N(4)#2 | 89.4(2) | O(5)-Cu(2)-N(2)#1 | 92.6(2) |
| O(5)-Cu(2)-N(4)#2 | 93.2(3) | N(2)#1-Cu(2)-N(4)#2 | 168.0(3) |

symmetry codes: #1 = 1-x, y, 1-z; #2 = 2-x, y, 2-z.