

Supplemental Information for

(3,4)-Connected jph-type Porous Framework with Cu₄I₄ clusters as jointing points of helices

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1. Experimental details:

Elemental analyses were performed on a Vario EL III elemental analyzer. The Fourier transform IR spectrum was obtained on a Perkin-Elmer Spectrum-one instrument using KBr pellets in the range of 4000–400 cm⁻¹. ¹H NMR (500MHz) chemical shifts were measured on a Varian Unity-500 spectrometer. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'pert pro X-ray diffraction with graphite-monochromatized Cu K α radiation (λ = 1.542 Å). Photoluminescence analysis was performed on an Edinburgh FLS920 fluorescence spectrometer. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were carried out on a NETZSCH STA449c system at a heating rate of 10°C min⁻¹ under a N₂ atmosphere.

Synthesis of 4-amino-3,5-bis(hydromethyl)-1,2,4-triazole (H₂ahmt). Glycolic acid (15.6 g, 0.2 mol) was mixed with hydrazine monohydrate (20.2 g, 0.4 mol, 20 ml) in a flask and the mixture was refluxed for 5 hours in an oil bath at 180°C. After cooling to room temperature the colorless compound were collected by filtering the mixture and then were recrystallized from water, yielding colorless crystals of H₂ahmt. Yield: 5.8 g (40% base on glycolic acid). Anal. Calcd for C₄H₈N₄O₂: C, 33.33; H, 5.56; N, 38.89. Found: C, 33.31; H, 5.52; N, 38.90. IR spectrum (KBr pellets, cm⁻¹): 3347s, 3184s, 2887s, 2698w, 1645s, 1519m, 1479m, 1462s, 1441m, 1352s, 1306s, 1205s, 1069s, 1029s, 1019m, 977s, 953m, 877m, 819m, 776m, 721w, 498m. δ_{H} (500 MHz, DMSO): 5.81 (2H, s, NH₂), 5.38 (1H, s, OH), 4.54 (2H, s, CH₂).

Solvent molecule sorption properties for compound **1**.

Single crystals of **1** were put into CH₃OH for three days at room temperature. The shape and transparency of the single crystals did not change during the experiments. X-ray analysis of the single crystal from the CH₃OH was given the same crystal data.

20 mg samples of **1** were put into CH₃CN for three days at room temperature. The new samples of **1** were collected by filtering the mixture and then were placed in air about several minutes. They were rapidly characterized by IR spectrum without drying in the desiccator. IR spectrum (KBr pellets, cm⁻¹): 3360 (br), 2975 (w), 1574 (s), 1415(s), 1090 (s), 1050(s), 925(w), 652(br). There is no band in the 2000~2200 cm⁻¹. And the difference is little between the origin samples and the immersed ones. So the compound may be not adsorbed CH₃CN at the temperature.

The experimental procedure about DMSO adsorption was same as CH₃CN adsorption. IR spectrum (KBr pellets, cm⁻¹): 3400 (br), 2975 (w), 1574 (vs), 1415 (s), 1099 (s), 1019 (s), 925 (w), 652 (br). There is little difference for the IR spectrum of compound before and after the experiment. So the compound may be not adsorbed DMSO at the room temperature.

In conclude, this porous compound may not adsorbed small solvent molecule such as CH₃OH, CH₃CN and DMSO at the temperature.

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers 653271 and 653270 for complexes **H₂ahmt** and **1**. Copies of this information may be obtained from The Director, CCDC, 12 union road, CB2 1EZ, UK (fax: +44-1233-336033; email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

2. The structure of drawings:

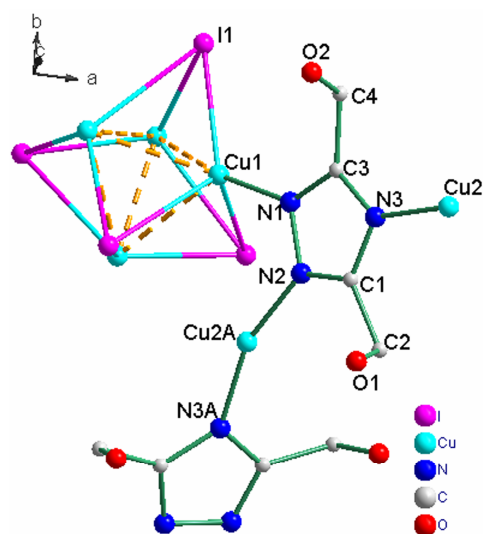


Figure S1. The coordination environments of Cu1 and Cu2 atoms in **1**. Symmetry codes: (A) $0.75 - y, 0.25 + x, 0.25 + z$.

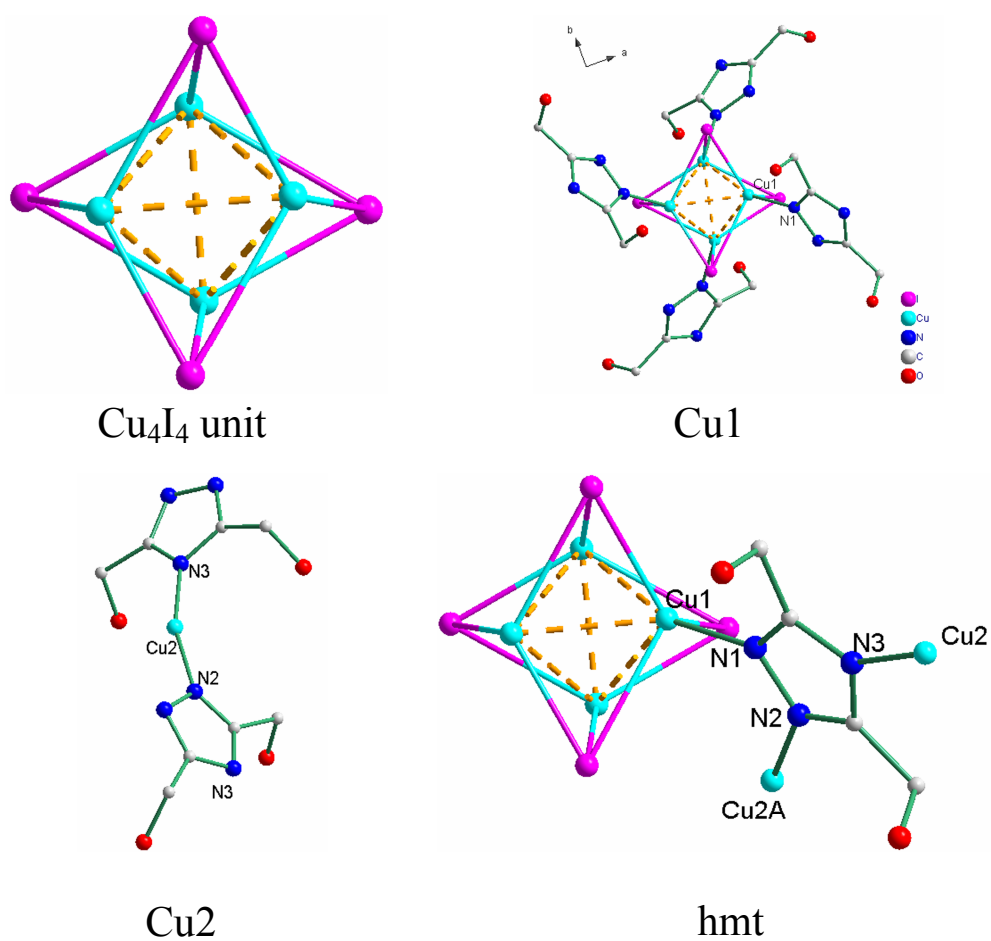


Figure S2. The coordination geometries of Cu₄I₄ unit, Cu1, Cu2, amt in compound **1**.

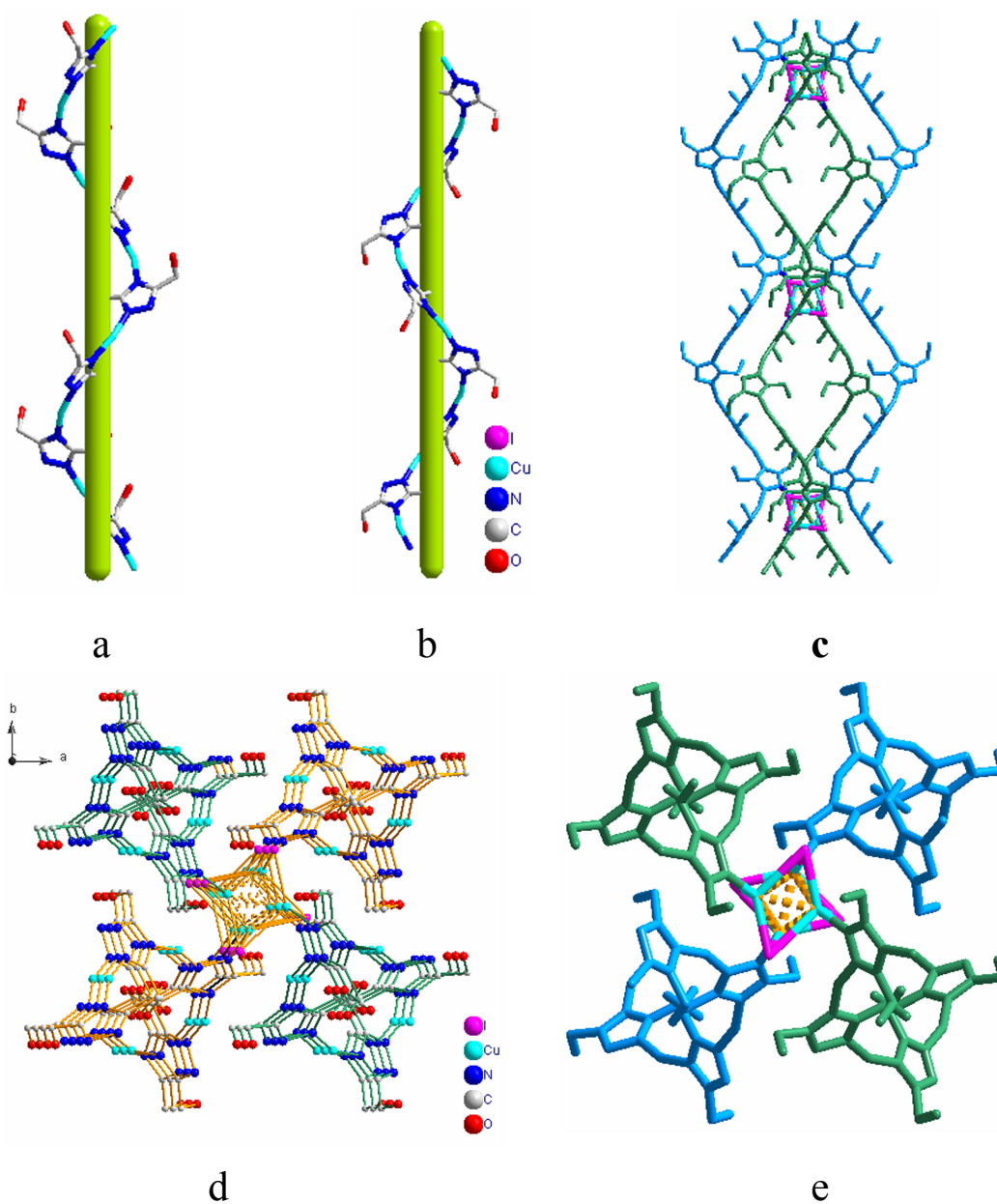


Figure S3. a) View of the right-handed helices. b) View of the left-handed helices. (c) View of four helices with opposite chiralities, blue (right-handed helices) sea green (left-handed helices)d) Ball and Stick view of four helices with opposite chiralities. e) Wires view of four helices with opposite chiralities along the c-axis.

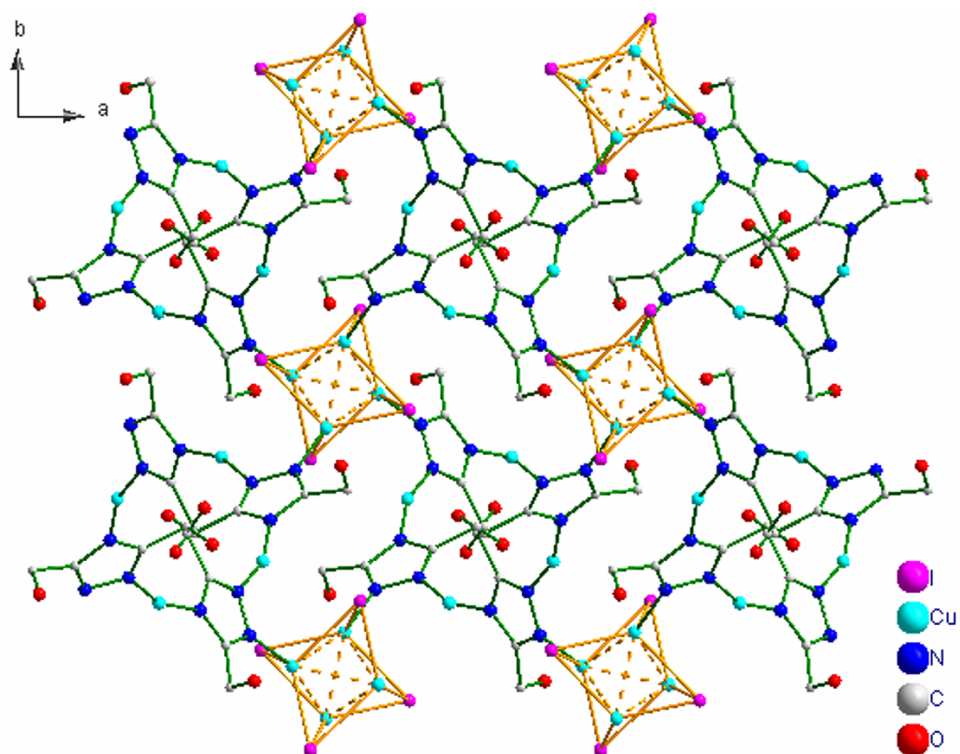


Figure S4. View of the 3D network down the *c*-axis for **1**

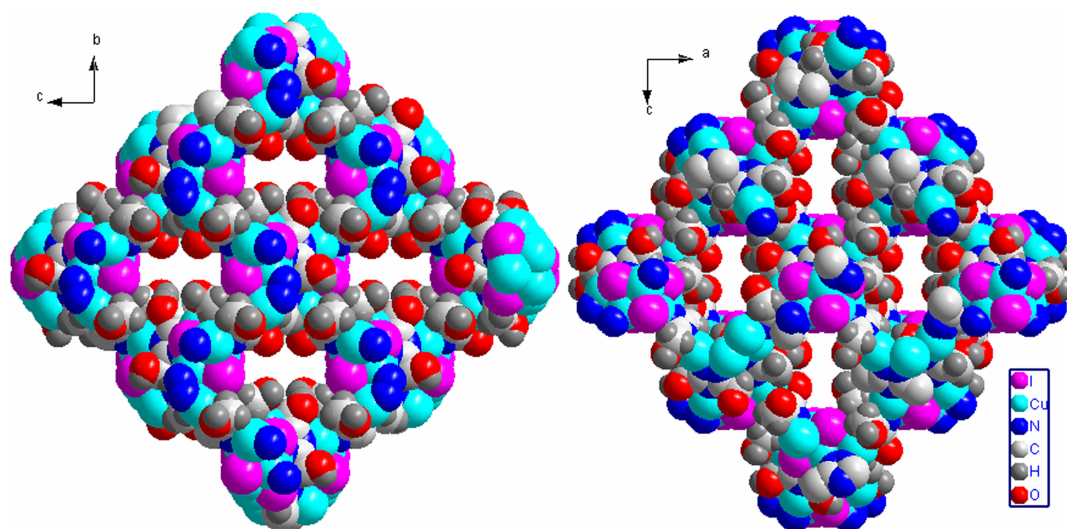


Figure S5. (a) Space filling model of the channel structures along the *a* axis. (b) Along the *b* axis.

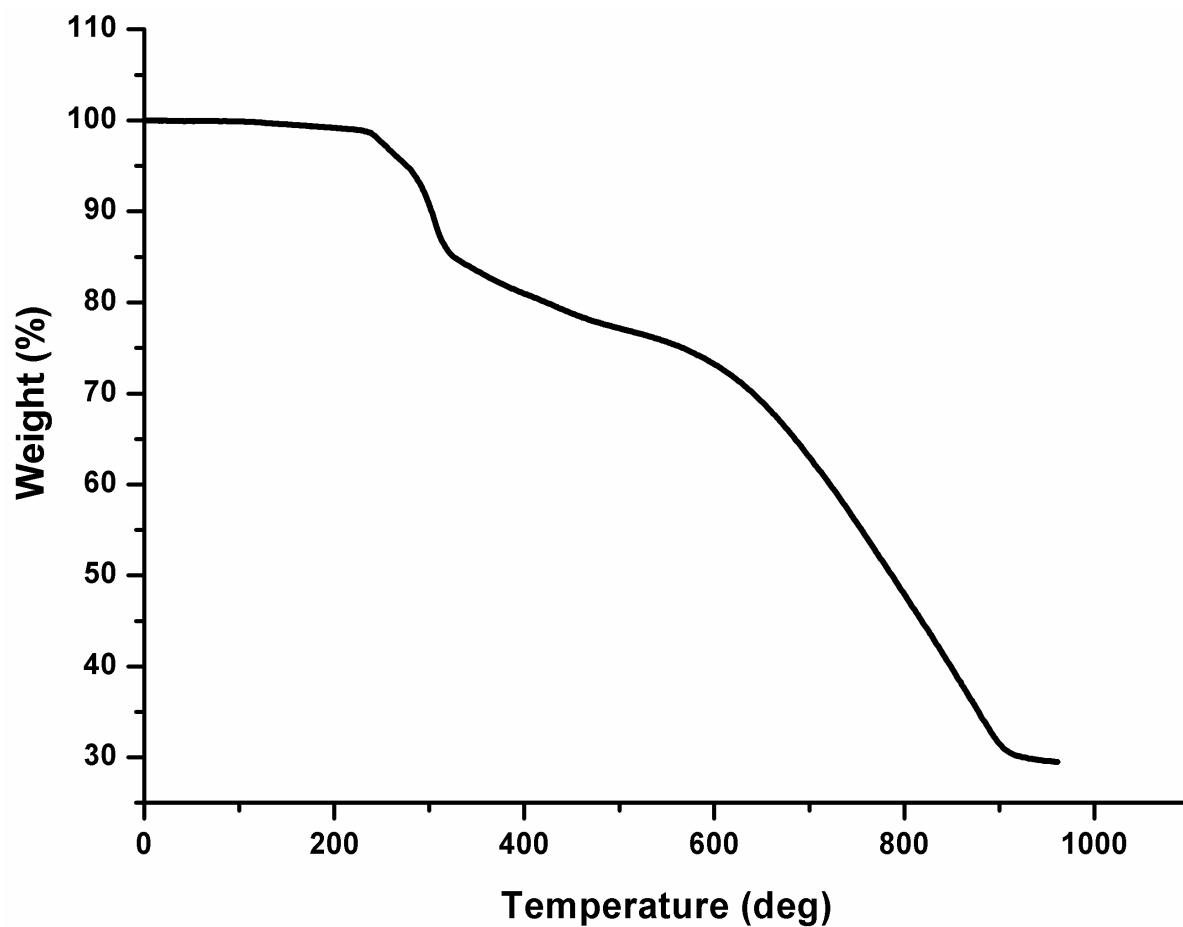


Figure S6. The TGA plot for complex 1.

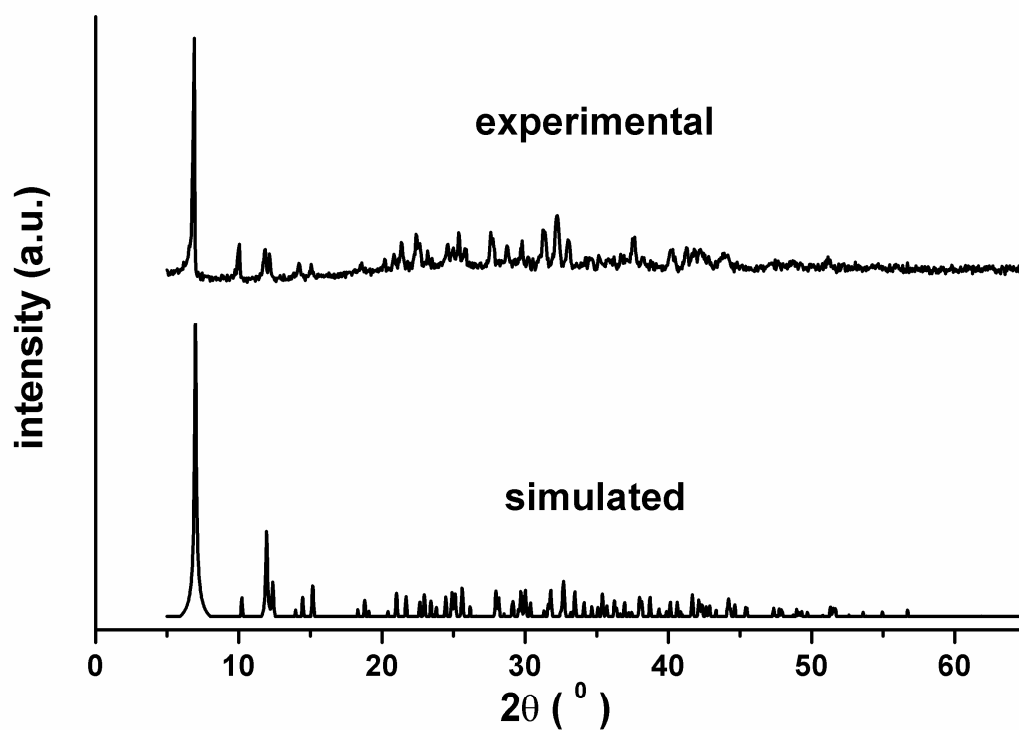


Figure S7. XRD patterns for complex 1.

Table 1S. Crystal and Structure Refinement Data for **1** and **H₂ahmt**.

complex	1	H₂ahmt
formula	C ₄ H ₆ Cu ₂ IN ₃ O ₂	C ₄ H ₈ N ₄ O ₂
f _w	382.10	144.14
cryst size	0.25 × 0.20 × 0.20	0.60 × 0.50 × 0.50
cryst color	pale-yellow	colorless
cryst syst	tetragonal	orthorhombic
space group	I4 ₁ /a	Pbca
<i>a</i> (Å)	17.3064(8)	8.7902(4)
<i>b</i> (Å)	17.3064(8)	16.0524(8)
<i>c</i> (Å)	18.5975(16)	16.0524(8)
<i>V</i> (Å ³)	5570.2(6)	1250.83(10)
<i>Z</i>	16	8
θ for data collection (deg)	2.19-27.48	2.30-27.48
reflns collected	3187	1421
<i>d</i> _{calcd} (g cm ⁻³)	1.823	1.531
<i>T</i> (K)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073
<i>F</i> (000)	2848.0	608.0
abs coeff (mm ⁻¹)	5.246	0.124
R1 ^a , wR2 ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0662 0.2045	0.0611 0.2050
R1, wR2 (all data)	0.0753 0.2166	0.0671 0.2070

$$^a R1 = \sum (| |Fo| | - |Fc| |) / \sum |Fo|, \quad ^b wR2 = \{ \sum w(Fo^2 - Fc^2)^2 / \sum w[(Fo^2)^2] \}^{1/2}$$

Table 2S. Selected Bond Lengths (Å) and Angels (deg) for **1**^a

Cu(1)-I(1)	2.5765(13)	Cu(1)-N(1)	1.971(6)
Cu(1)-I(1)#2	2.8321(14)	Cu(2)-N(2)#4	1.873(6)
Cu(1)-I(1)#3	2.7077(13)	Cu(2)-N(3)	1.877(6)
Cu(1)-I(1)-Cu(1)#1	64.09(4)	I(1)-Cu(1)-I(1)#3	112.46(5)
Cu(1)-I(1)-Cu(1)#2	57.95(4)	N(1)-Cu(1)-I(1)#2	93.5(2)
Cu(1)#1-I(1)-Cu(1)#2	60.81(4)	I(1)-Cu(1)-I(1)#2	119.13(4)
N(1)-Cu(1)-I(1)	119.11(18)	I(1)#3-Cu(1)-I(1)#2	104.91(4)
N(1)-Cu(1)-I(1)#3	105.26(19)	N(2)#4-Cu(2)-N(3)	160.8(3)

Symmetry transformations used to generate equivalent atoms: #1, -*y* + 5/4, *x* + 1/4, -*z* + 5/4; #2, -*x* + 1, -*y* + 3/2, *z* + 0; #3, *y* - 1/4, -*x* + 5/4, -*z* + 5/4; #4, *y* - 1/4, -*x* + 3/4, *z* - 1/4.