Supplementary Material (ESI) for CrystEngComm

Positional Disorder of Cu(II) ion in Cluster: A Novel Heptanuclear Cu(II) Core Supported by 4-Bromo-3,5-dimethylpyrazolate

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I. Experimental Section.

1. Materials and Methods: The C, H, and N elemental analyses were conducted on Perkin-Elmer 240C elemental analyzer and inductively coupled plasma analysis on a Perkin-Elmer Optima 3300DV ICP spectrometer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on Nicolet 170 SXFT/IR spectrometer. XPRD (X-ray powder diffraction) of samples were collected on Japan Rigaku D/max γA X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ =0.154060 nm). XPS analysis was performed on an AXIS ULTRA spectrometer with an Al Kα achromatic X-ray source. TGA curves were performed on a 2960 SDT simultaneous thermal analyzer from room temperature to 900 °C with a heating rate of 10 °C / min under nitrogen atmosphere.Variable temperature susceptibility measurements were carried out in the temperature range 2–300 K at an applied magnetic field of 5 kOe on polycrystalline samples with a Quantum Design MPMS-5 magnetometer. The experimental susceptibilities were corrected for the Pascal's constants. Hydrothermal syntheses were carried out in 15 mL Teflon-lined autoclaves under autogenous pressure.

2. Synthesis of compound **1**: A mixture of CuCl (0.1007g, 1mmol) and bdpz (0.1305g, 0.75mmol) was dissolved in 15mL DMF with continuous stirring, then transferred into a Teflon container and kept at 90°C for 48h in an oven. After cooled down to room temperature naturally, the mixture was filtered and allowed to evaporate at room temperature. About a month later, fine green distorted tetragonal pyramid-like crystals were filtered off, washed with distilled water, and dried at room temperature to give a yield of 25 % based on Cu. Anal. Calc. for $C_{54}H_{96}Br_6Cl_4Cu_7N_{20}O_{12}$ (%): C, 28.40; N, 12.27; H, 4.24; Cu, 19.48; Found: C, 28.22; N, 12.10; H, 4.52;

Cu, 19.00; IR (cm^{-1}): 3546(w), 3346(br), 2923(m), 1649(vs), 1510(m), 1434(m), 1412(m), 1371(m), 1339(m), 1254(w), 1154(w), 1104(vs), 1059(vw), 777(vw), 779(w), 689(m).

3. Synthesis of compound **2**: Compound **2** was synthesized in an analogous way to **1** but using solvent DMAC instead of DMF. Green rod-like crystals of **2** were obtained finally with a yield of 13% or so. Anal. Calcd. For $C_{50}H_{85}Br_6Cl_4Cu_7N_{17}O_9$ (%):C, 31.08; N, 11.69; H, 4.71; Cu, 18.57; Found: C, 31.05; N, 11.39; H, 4.98; Cu, 18.23; IR (cm^{-1}): 3549(w), 3256(br), 2921(m), 1601(vs), 1509(s), 1419 (s), 1338 (m), 1260 (w), 1100 (vs), 1023(m),777 (m), 452(m).

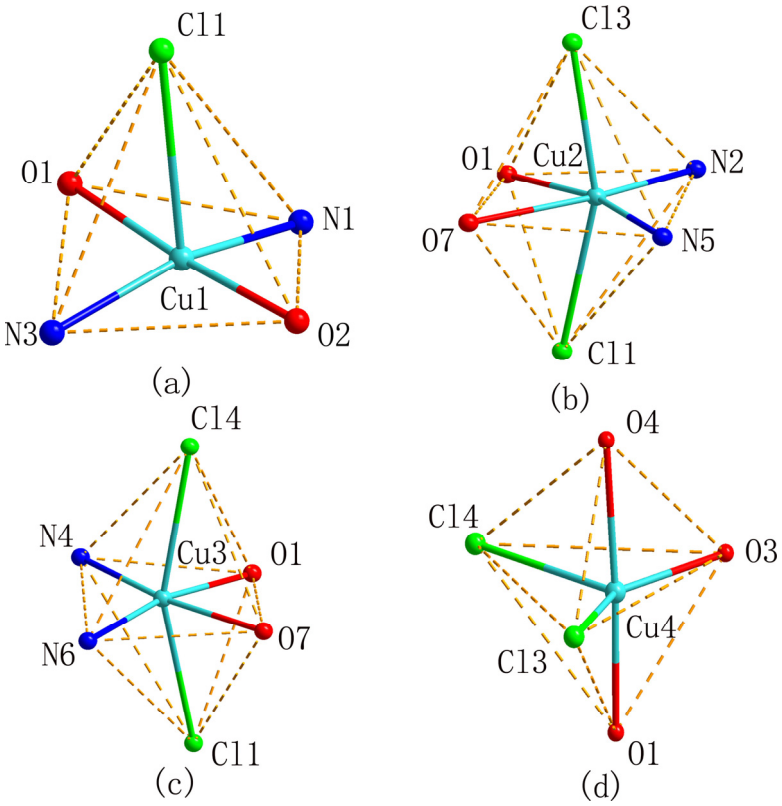
4. No estimated standard deviations were given for the listed hydrogen bonds in complex **2** in Figure 3 for the reason that the oxygens of the uncoordinated DMAC and water molecule are not crystallographically well defined for crystallographically disorder.

5. The CuCl is oxidized to Cu(II) complex under the solvate thermal condition in our experiments. Its oxidation state can be confirmed from Bond valence sum calculation (Table S1). The average empirical valence of all Cu atoms is 1.747 in **1**, 1.899 in **2**, indicating the oxidation state of Cu is both +2 in two complexes.When $CuCl_2$ is employed instead of CuCl, we also can obtain **1** and **2** but in polycrystalline shape.

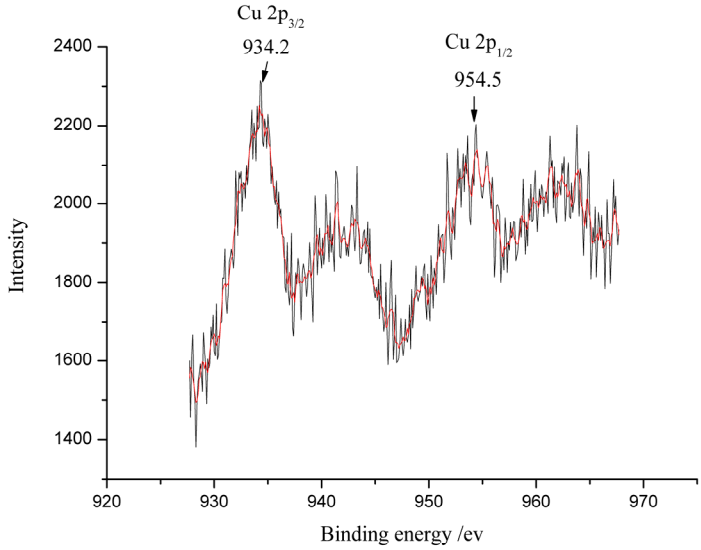
II. Table S1. The BVS calculation result on Cu atoms in complexes **1** and **2.**

Code	**Bond Valence**	
	Complex **1**	Complex **2**
Cu1	1.785	1.701
Cu2	1.632	1.798
Cu3	1.711	1.723
Cu4	1.862	2.373
The mean values	1.747	1.899

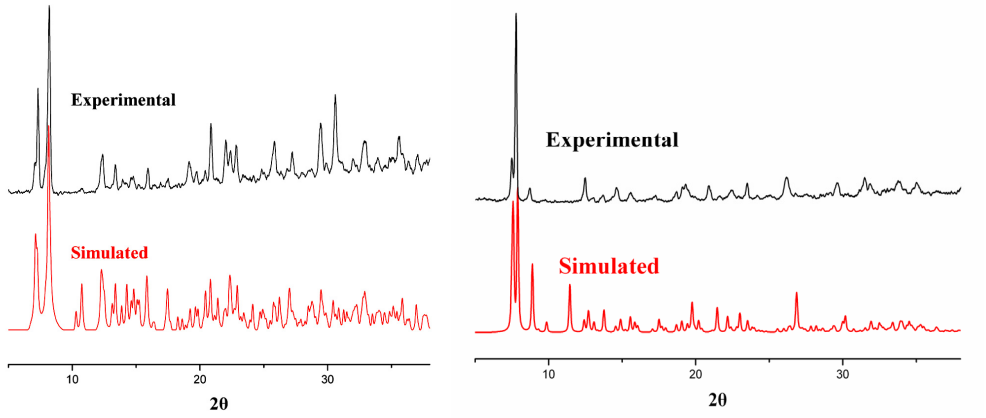
III. **Figure S1.** The coordination geometric frameworks of the Cu1, Cu2, Cu3 and Cu4 ions in **1**.



IV. **Figure S2.** XPS spectra of **1** for Cu $2p_{3/2}$ and Cu $2p_{1/2}$.

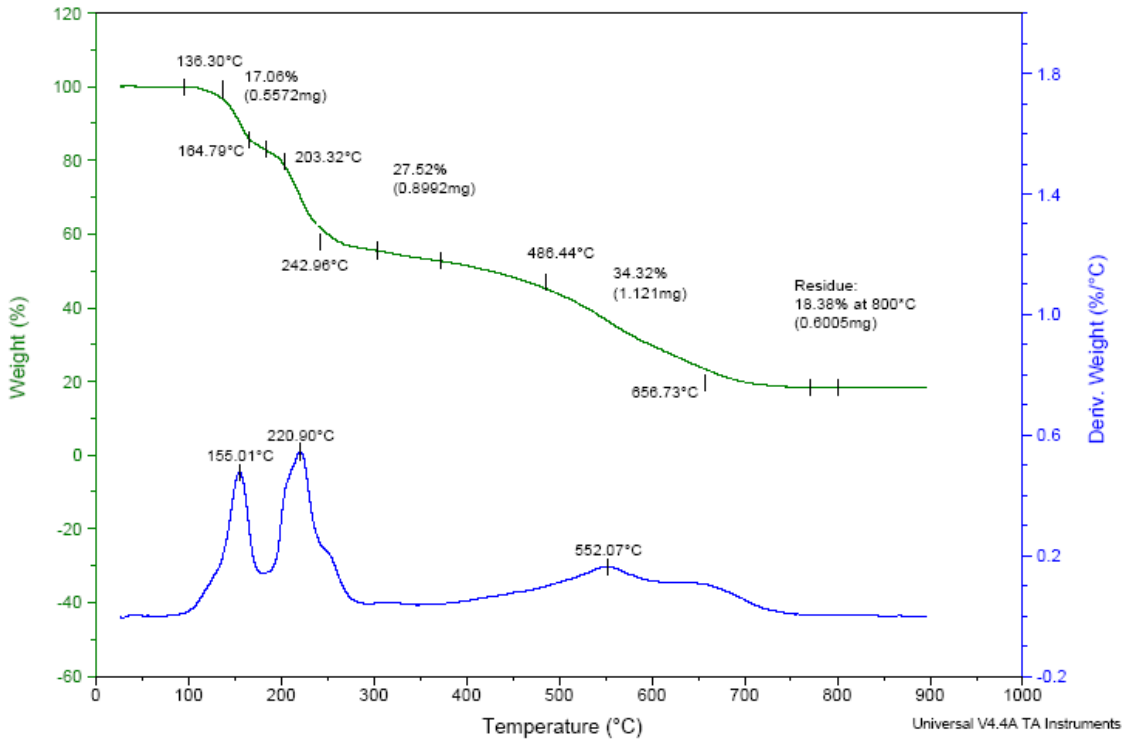


V. Figure S3. X-ray powder diffraction patterns. Black: experimental data; Red: simulated patterns from single-crystal X-ray structure data: (a) for **1,** (b) for **2.**



(a) (b)

VI. Figure S4. Thermal analysis curve of complex **1:**



It is necessary to mention that it is difficult to completely pick out all the interstitial solvent molecules in **1** from the electronic map of X-ray diffraction, so we finally estimate the number of interstitial DMF in **1** to be 4 according to the thermogravimetric analysis and elemental microanalysis data except the H-bonding DMF molecule discussed in the context. The TG-DTA curves of **1** shows two steps of weight loss (Figure S4), giving a tatal loss of 81.62 % in the range of 25-900°C. At

first, the sample keep unchanged before 136 °C, then an initial weight loss of 17.06 % ascribed to the release of five interstitial solvent molecules and one coordination water molecule(O4) per formula units (calcd 16.78%) occurs from 136.9 to 164.8 °C, and one intense endothermal peak at 155.01 is observed in the corresponding DTA curve. The second weight loss of 64.56% from 164.8 °C to 800 °C is assigned to the combustion of three coordinated DMF molecules, six bdpz ligand, four Cl ions (calcd. 64.35 %); and two endothermal peaks at 220.9 and 552.07 °C are observed in the corresponding DTA curve.

VI. Table S2. Selected Bond lengths [Å] and angles [°] for **1**.

Bond lengths			
Cu(1)-N(3)	1.965(3)	Cu(4) -O(1)	1.965(2)
Cu(1)-O(1)	1.9867(16)	Cu(4) -Cl(3)	2.3947(16)
Cu(1)-O(2)	2.002(2)	Cu(4) -O(3)	1.892(4)
Cu(1)-Cl(1)	2.6862(10)	Cu(4)-O(4)	2.1464(17)
Cu(1)-N(1)	1.9715(17)	Cu(4)-Cl(4)	2.5095(18)
O(1)-Cu(2)	1.9259(17)	Cu(3)-Cl(4)	2.7648(14)
Cu(2)-N(2)	2.001(3)	Cu(3)-O(1)	1.9404(17)
Cu(2)-O(7)	2.234(2)	Cu(3)-N(4)	1.965(1)
Cu(2)-Cl(3)	2.6807(11)	Cu(3)-O(7)	2.134(2)
Cu(2)-N(5)	1.9420(15)	Cu(3)-N(6)	1.945(3)
Cu(2)-Cl(1)	2.8218(11)	Cu(3)- Cl(1)	2.8196(10)
Cu(2)…Cu(4)	3.0372(12)		
Cu(2)…Cu(3)	2.9226(6)		
Bond angles			
N(3)-Cu(1)-O(1)	88.47(9)	O(1)-Cu(3)-N(6)	167.93(10)
N(3)-Cu(1)-O(2)	93.20(11)	O(1)-Cu(3)-O(7)	83.67(9)
O(1)-Cu(1)-O(2)	175.11(10)	N(6)-Cu(3)-O(7)	86.42(11)
N(3)-Cu(1)-Cl(1)	98.34(9)	O(1)-Cu(3)-Cl(4)	85.42(6)
O(1)-Cu(1)-Cl(1)	78.08(5)	N(6)-Cu(3)-Cl(4)	100.46(9)
O(2)-Cu(1)-Cl(1)	97.12(8)	O(7)-Cu(3)-Cl(4)	84.23(8)
O(1)-Cu(2)-N(2)	89.11(9)	O(3)-Cu(4)-O(1)	94.25(15)
O(1)-Cu(2)-O(7)	81.36(9)	O(3)-Cu(4)-O(4)	88.83(14)
N(2)-Cu(2)-O(7)	170.46(11)	O(1)-Cu(4)-O(4)	176.71(8)
O(1)-Cu(2)-Cl(3)	88.15(6)	O(3)-Cu(4)-Cl(3)	137.28(14)
N(2)-Cu(2)-Cl(3)	95.30(9)	O(1)-Cu(4)-Cl(3)	95.90(7)
O(7)-Cu(2)-Cl(3)	84.20(7)	O(4)-Cu(4)-Cl(3)	82.58(6)
Cu(3)-O(7)-Cu(3)#1	92.19(12)	O(3)-Cu(4)-Cl(4)	108.03(14)
Cu(3)-O(7)-Cu(2)	83.97(3)	O(1)-Cu(4)-Cl(4)	92.30(7)
Cu(3)#1-O(7)-Cu(2)	155.96(16)	O(4)-Cu(4)-Cl(4)	85.64(6)
Cu(2)-O(7)-Cu(2)#1	89.94(11)	Cl(3)-Cu(4)-Cl(4)	112.87(5)

Cu(2)-O(1)-Cu(3)	98.21(8)	Cu(4)#1-Cl(3)-Cu(4)	62.03(6)
Cu(2)-O(1)-Cu(4)	102.64(8)	Cu(4)#1-Cl(3)-Cu(2)#1	73.27(4)
Cu(2)-O(1)-Cu(1)	105.33(8)	Cu(4)-Cl(3)-Cu(2)#1	108.61(6)
Cu(3)-O(1)-Cu(1)	103.93(8)	Cu(4)-Cl(3)-Cu(2)	73.27(4)
Cu(4)-O(1)-Cu(1)	133.42(9)	Cu(2)#1-Cl(3)-Cu(2)	72.16(4)
Cu(4)-Cl(4)-Cu(3)#1	105.18(6)	Cu(3)#1-Cl(4)-Cu(3)	67.57(4)
Cu(4)-Cl(4)-Cu(3)	73.43(4)	Cu(4)#1-O(4)-Cu(4)	70.19(8)
Cu(4)#1-Cl(4)-Cu(3)	105.18(6)		

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1/2,z

VII. Table S3. Selected Bond lengths [Å] and angles [°] for **2**.

Cu(1)-O(6)#1	1.948(3)	O(6)-Cu(3)	1.994(4)
Cu(1)-N(1)	1.956(4)	Cl(2)-Cu(3)	2.7065(16)
Cu(1)-N(6)#1	1.982(4)	Cu(3)-N(5)	1.977(4)
Cu(1)-O(1)	2.1346(13)	Cu(3)-N(4)	1.998(4)
Cu(1)-Cl(3)	2.6718(14)	Cu(3)-O(4)	2.003(4)
O(1)-Cu(2)	2.2340(12)	Cl(3)-Cu(4)	2.2810(19)
O(6)-Cu(2)	1.933(3)	Cu(4)-O(2)	1.886(5)
Cu(2)-N(2)	1.946(5)	Cu(4)-O(3)#1	2.233(7)
Cu(2)-N(3)	2.007(4)	Cu(4)-Cl(3)#1	2.5665(15)
Cu(2)-Cl(3)	2.6218(15)	Cu(4)-O(6)	1.998(4)
Cu(2)-Cl(2)	2.7272(16)	O(3)-Cu(4)	1.947(7)
Cu(1)…Cu(2)#1	2.9128(9)		
Cu(2) …Cu(4)	3.0128(14)		
Cu(1) …Cu(3)	3.093(1)		
O(6)#1-Cu(1)-N(1)	169.48(17)	O(3)#1-O(3)-Cu(4)	103.6(7)
O(6)#1-Cu(1)-N(6)#1	87.88(15)	O(3)#1-O(3)-Cu(4)#1	57.9(6)
N(1)-Cu(1)-N(6)#1	98.97(18)	Cu(4)-O(3)-Cu(4)#1	72.7(2)
O(6)#1-Cu(1)-O(1)	85.27(13)	N(5)-Cu(3)-O(6)	87.40(15)
N(1)-Cu(1)-O(1)	88.01(17)	N(5)-Cu(3)-N(4)	162.20(19)
N(6)#1-Cu(1)-O(1)	173.01(16)	O(6)-Cu(3)-N(4)	87.79(15)
O(6)#1-Cu(1)-Cl(3)	90.57(10)	N(5)-Cu(3)-O(4)	92.56(16)
N(1)-Cu(1)-Cl(3)	96.63(13)	O(6)-Cu(3)-O(4)	178.57(15)
N(6)#1-Cu(1)-Cl(3)	95.72(14)	N(4)-Cu(3)-O(4)	92.68(15)
O(1)-Cu(1)-Cl(3)	82.95(12)	N(5)-Cu(3)-Cl(2)	101.03(13)
O(6)#1-Cu(1)-Cu(2)#1	41.16(10)	O(6)-Cu(3)-Cl(2)	77.96(10)
N(1)-Cu(1)-Cu(2)#1	129.06(14)	N(4)-Cu(3)-Cl(2)	94.70(13)
N(6)#1-Cu(1)-Cu(2)#1	124.48(11)	O(4)-Cu(3)-Cl(2)	100.65(12)
O(1)-Cu(1)-Cu(2)#1	49.66(3)	O(2)-Cu(4)-O(3)	86.3(3)
Cl(3)-Cu(1)-Cu(2)#1	103.26(4)	O(2)-Cu(4)-O(6)	92.02(18)
O(6)-Cu(2)-N(2)	168.70(16)	O(3)-Cu(4)-O(6)	177.3(2)
O(6)-Cu(2)-N(3)	87.72(16)	O(2)-Cu(4)-O(3)#1	92.5(2)

N(2)-Cu(2)-N(3)	102.40(17)	O(3)-Cu(4)-O(3)#1	18.5(3)
O(6)-Cu(2)-O(1)	82.95(12)	O(6)-Cu(4)-O(3)#1	164.0(2)
N(2)-Cu(2)-O(1)	87.09(14)	O(2)-Cu(4)-Cl(3)	135.04(14)
N(3)-Cu(2)-O(1)	170.41(16)	O(3)-Cu(4)-Cl(3)	83.3(2)
O(6)-Cu(2)-Cl(3)	87.84(11)	O(6)-Cu(4)-Cl(3)	96.49(11)
N(2)-Cu(2)-Cl(3)	96.13(14)	O(3)#1-Cu(4)-Cl(3)	91.1(2)
N(3)-Cu(2)-Cl(3)	95.23(14)	O(2)-Cu(4)-Cl(3)#1	112.80(13)
O(1)-Cu(2)-Cl(3)	82.30(12)	O(3)-Cu(4)-Cl(3)#1	90.05(18)
O(6)-Cu(2)-Cl(2)	78.39(11)	O(6)-Cu(4)-Cl(3)#1	92.55(10)
N(2)-Cu(2)-Cl(2)	95.41(15)	O(1)-Cu(2)-Cl(2)	84.60(10)
N(3)-Cu(2)-Cl(2)	95.67(14)	Cl(3)-Cu(2)-Cl(2)	162.05(4)
Cu(3)-Cl(2)-Cu(2)	69.56(4)		
Cu(1)-O(1)-Cu(1)#1	155.9(3)	Cu(3)-O(6)-Cu(4)	139.77(18)
Cu(1)-O(1)-Cu(2)#1	83.60(6)	Cu(4)-Cl(3)-Cu(4)#1	61.39(6)
Cu(1)#1-O(1)-Cu(2)#1	91.58(6)	Cu(4)-Cl(3)-Cu(2)	75.48(5)
Cu(1)-O(1)-Cu(2)	91.58(6)	Cu(4)#1-Cl(3)-Cu(2)	108.78(5)
Cu(1)#1-O(1)-Cu(2)	83.60(6)	Cu(4)-Cl(3)-Cu(1)	109.54(5)
Cu(2)#1-O(1)-Cu(2)	156.8(3)	Cu(4)#1-Cl(3)-Cu(1)	72.55(4)
Cu(2)-O(6)-Cu(1)#1	97.29(15)	Cu(2)-Cl(3)-Cu(1)	72.55(4)
Cu(2)-O(6)-Cu(3)	104.23(14)	Cu(2)-O(6)-Cu(4)	100.05(16)
Cu(1)#1-O(6)-Cu(3)	104.59(16)	Cu(1)#1-O(6)-Cu(4)	103.55(14)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2