Supporting Information

"$[(C_2H_5)_3NH]_2Cu_2(C_2O_4)_3$: A Three-Dimensional Metal-Oxalato Framework Showing Structural Related Dielectric and Magnetic Transitions at Around 165 K"

by B. Zhang et al

365.7 mg $Cu(NO_3)_2{\cdot}2H_2O$ (1.6 mmol) was dissolved into 10.0ml H_2O. Meanwhile, $H_2C_2O_4{\cdot}2H_2O$ 376.3 mg (3.0 mmol) was dissolved into 10.0 ml H_2O, then 604 mg Et_3N (6.0 mmol) was added. The solution was added into the solution of $Cu(NO_3)_2$. Muddy liquor was obtained. The mixture was filtered and filtrate was remained in room-temperature. Blue-diamond crystal was appeared on the bottom of baker after three weeks. 280.0 mg crystal was collected and washed with water quickly and dried in air. The yield is 63%. Elemental analysis: $C_{18}H_{32}O_{12}N_2Cu_2$, calc. C 36.30, H 5.42, N 4.70; exp. C 36.41, H 5.42, N 4.76. IR on KBr pellet (cm^{-1}): 3403(bw), 2976(w), 2938(m), 2739(m), 2678(m), 2491(w), 1672(s), 1639(s), 1606(s), 1457(m), 1417(m), 1361(w), 1289(m), 1171(w), 1035(w), 804(m), 489(m), 412(w).

IR experiment was performed on Bio-rad FTS6000 with KBr pellet. Thermogravimetric analysis was carried out on Shimadzu DTG-60 Analyzer with 10ºC/min from room-temperature to 600ºC. Powder X-ray diffraction pattern was obtained on a Rigaku RINT2000 diffractometer at room temperature with Cu Kα (λ = 1.54056 Å) radiation in a flat-plate geometry. DSC experiment was performed on a TOLEDO DSC1 STAR with sweeping rate of 10°C/min under nitrogen atmosphere.

A piece of single crystal was selected for X-ray diffraction. Data was collected at 293 K, 180 K, 155 K and 135 K on Nonius Kappa CCD with Mo Kα (λ = 0.71073 Å) radiation.[1] The crystal structure was solved by direct method, hydrogen atoms of ethyl groups and N were found by calculation. All of nonhydrogen atoms were refined anisotropically.[2] The crystallographic data were listed on Table S1. The crystal discussion was performed with data of 135 K. Crystallographic data of **1** at 135 K: $C_{18}H_{32}Cu_2N_2O_{12}$, Mr = 595.54, monoclinic, space group $P\ 2_1/c$, a = 8.6987(1) Å, b = 34.1408(4) Å, c = 8.6081(1) Å, β = 107.578(1)º, V = 2437.07(5) $Å^3$, Z = 4, D_C = 1.623g·cm^{-3}, μ = 1.808 mm^{-1}, 27882

measured data, 5518 unique, R_{int} = 0.0368. R_1 = 0.0308 for 4832 observations of $I \geq 2\sigma(I_0)$, wR_2 = 0.0823 for all data, *GOF* = 1.101. CCDC-852903/6.

The dielectric measurements were performed on pellet of compressed crystal at TH2828 from 340 K to 113 K. The voltage is parallel with the thinnest direction of pellet.

Magnetization measurement was performed on polycrystalline sample tightly packed by parafilm inside a capsule on a Quantum Design MPMS 7 System. Magnetic susceptibility data was corrected for the diamagnetism of the sample by Pascal constant ($-136.5\times10^{-6}cm^3mol^{-1}$ per Cu), parafilm and capsule.[3]

Reference:

1. Otwinowski & Minor, *Denzo and Scalpack*, 1997.
2. G. M. Sheldrick, University of Göttingen, Göttingen(Germany), *SHELX-97*, 1997.
3. O. Kahn, *Molecular Magnetism*; John Wiely & Sons Inc., New York, 1993.

Table S1. Crystallographic data of **1** at 293K, 180 K, 155 K and 135 K

T, K	293	180	155	135
Cell parameters				
a, Å	8.8294(1)	8.7407(1)	8.7156(1)	8.6987(1)
b, Å	33.7719(4)	33.9886(4)	34.0813(4)	34.1408(4)
c, Å	8.8052(1)	8.6771(1)	8.6360(1)	8.6081(1)
β, º	107.901(1)	107.725(1)	107.632(1)	107.578(1)
V, Å^3	2498.48(5)	2455.46(5)	2444.22(5)	2437.07(5)
Space group	*P* 2_1/c	*P* 2_1/c	*P* 2_1/c	*P* 2_1/c
$T_{min.}$, $T_{max.}$,	0.582, 0.683	0.576, 0.682	0.590,0.681	0.584, 0.680
θ_{min}, θ_{max}, º	0.987, 27.51	0.984, 27.52	0.979, 27.54	0.982,27.54
Completeness,%	98.7	98.4	97.9	98.2
No. total reflns.	30048	28663	28252	27882
No. unique reflns. (R_{int})	5699(0.0422)	5569(0.0394)	5535(0.0284)	5518(0.0268)
No. obs. [I≥2σ(I_0)]	3688	4523	4667	4832
No. params.	340	332	340	319
Exti.	0.0036(5)	0.0025(4)	0.0026(4)	0.0026(4)
R, wR2 (I≥2σ(I_0))	0.0325, 0.0893	0.0321, 0.0842	0.0299,0.0775	0.0308,0.0802
R, wR2 (all data)	0.0593, 0.0965	0.0436,0.0885	0.0394, 0.0807	0.0371,0.0823
GOF	1.071	0.980	1.075	1.101
Δρ, e/Å^3	0.337(-0.265)	0.540(-0.421)	0.420(-0.332)	0.815(-0.373)
Max. and mean Δ/σ	0.001/0.000	0.001/0.000	0.001, 0.000	0.001,0.000
CCDC	852906	852905	852904	852903

Table S2. Hydrogen bonds in **1** at 135 K, 155 K, 180 K and 293 K.

T, K	Donor− H···Acceptor	D− H Å	H···A Å	D···A Å	D − H...A º
135	N(1) −H(1) ···O(9)	0.93	1.87	2.789(2)	170
	N(2) −H(2) ···O(5)	0.93	1.84	2.763(2)	170
155	N(1) −H(11) ···O(9)	0.93	1.87	2.789(2)	170
	N(2) −H(2) ···O(5)	0.93	1.84	2.762(2)	169
180	N(1) −H(1) ···O(9)	0.93	1.86	2.786(2)	170
	N(2) −H(2) ···O(5)	0.93	1.85	2.768(3)	169
293	N(1) −H(1) ···O(9)	0.91	1.90	2.789(2)	166
	N(2) −H(2) ···O(5)	0.91	1.89	2.784(3)	166

Table S3. Cu–O bond distance (Å) of **1** at different temperatures.

T, K	293	180	155	135
Cu1-O, Å	1.985(2), 1.993(2) 2.064(2), 2.083(2) 2.148(2), 2.148(2)	1.964(2), 1.978(2) 2.029(2), 2.004(2) 2.190(2),2.271(2)	1.957(2),1.975(2) 2.107(2),2.023(1) 2.209(1),2.304(2)	1.956(2),1.975(1) 2.003(1),2.006(1) 2.221(1),2.321(2)
Cu2-O, Å	1.974(2), 1.988(2) 2.070(2), 2.086(2) 2.170(2), 2.202(2)	1.960(2),1.987(2) 2.031(2), 2.034(2) 2.214(2), 2.258(2)	1.957(1), 1.989(1) 2.010(2), 2.014(2) 2.239(4), 2.293(2)	1.956(1), 1.989(1) 1.993(1), 1.998(2) 2.253(2), 2.311(2)

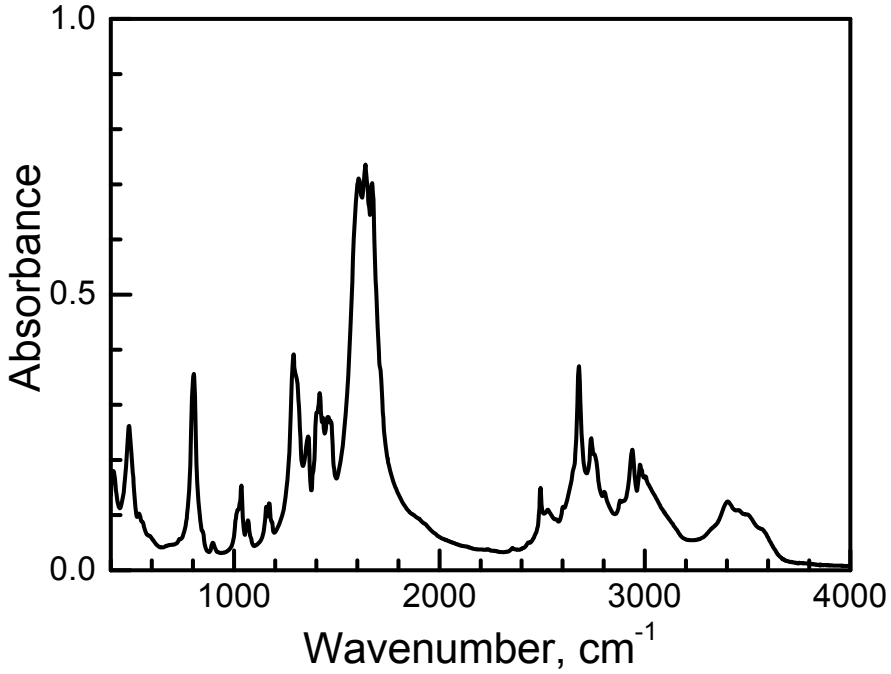


Figure S1. IR spectra of **1** at room-temperature.

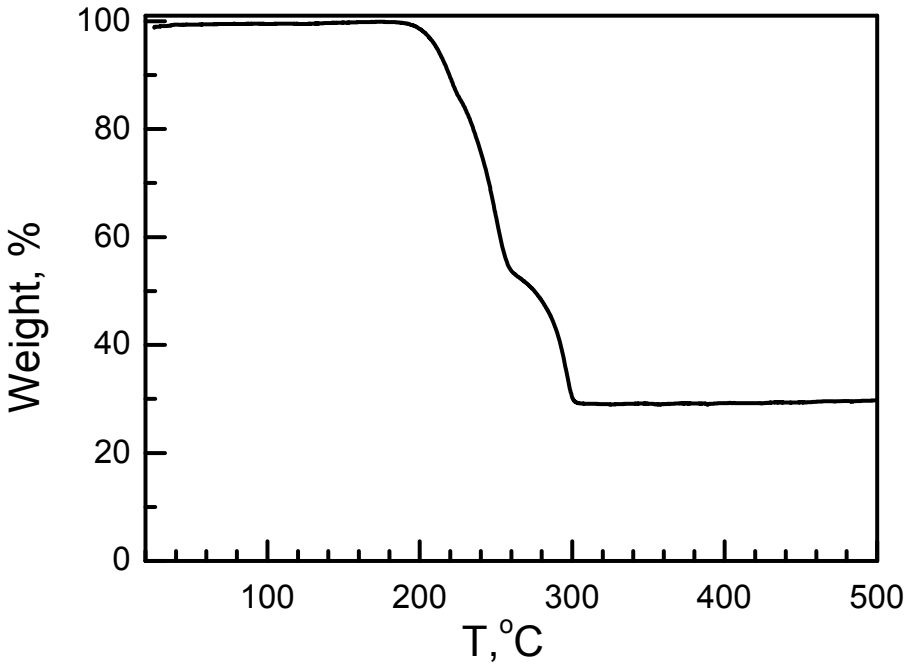


Figure S2. TGA plot of **1** with 10ºC/min..

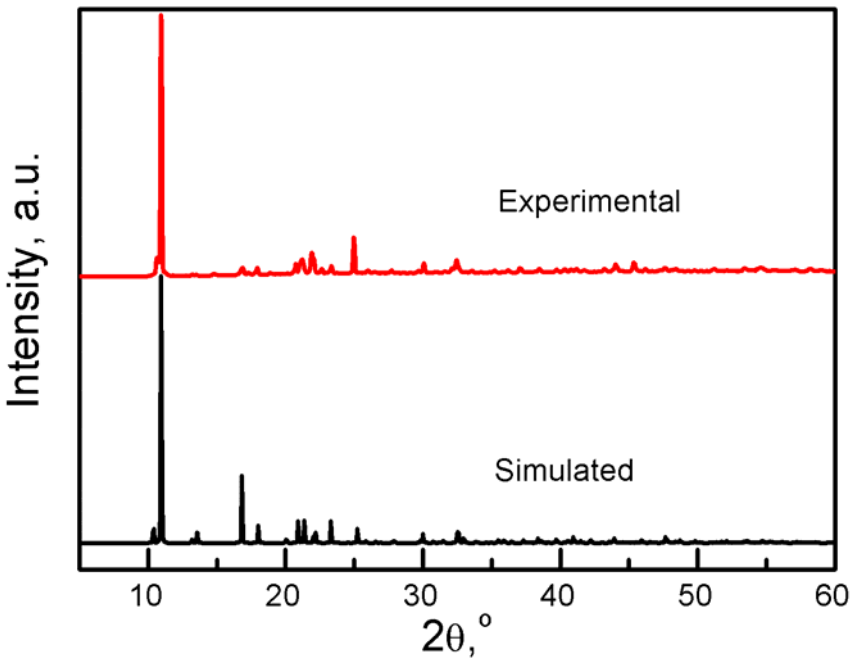


Figure S3. X-ray powder diffraction pattern of **1** at room-temperature.

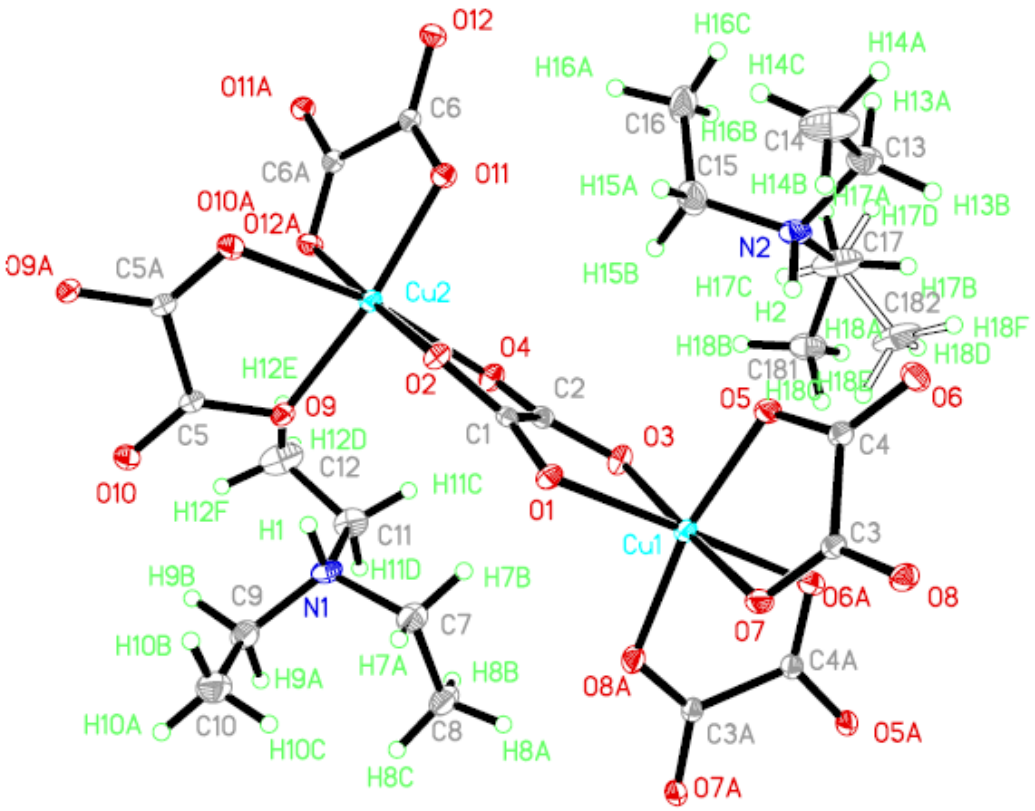


Figure S4. ORTEP drawing of **1** with 30% ellipsoid at 135 K.

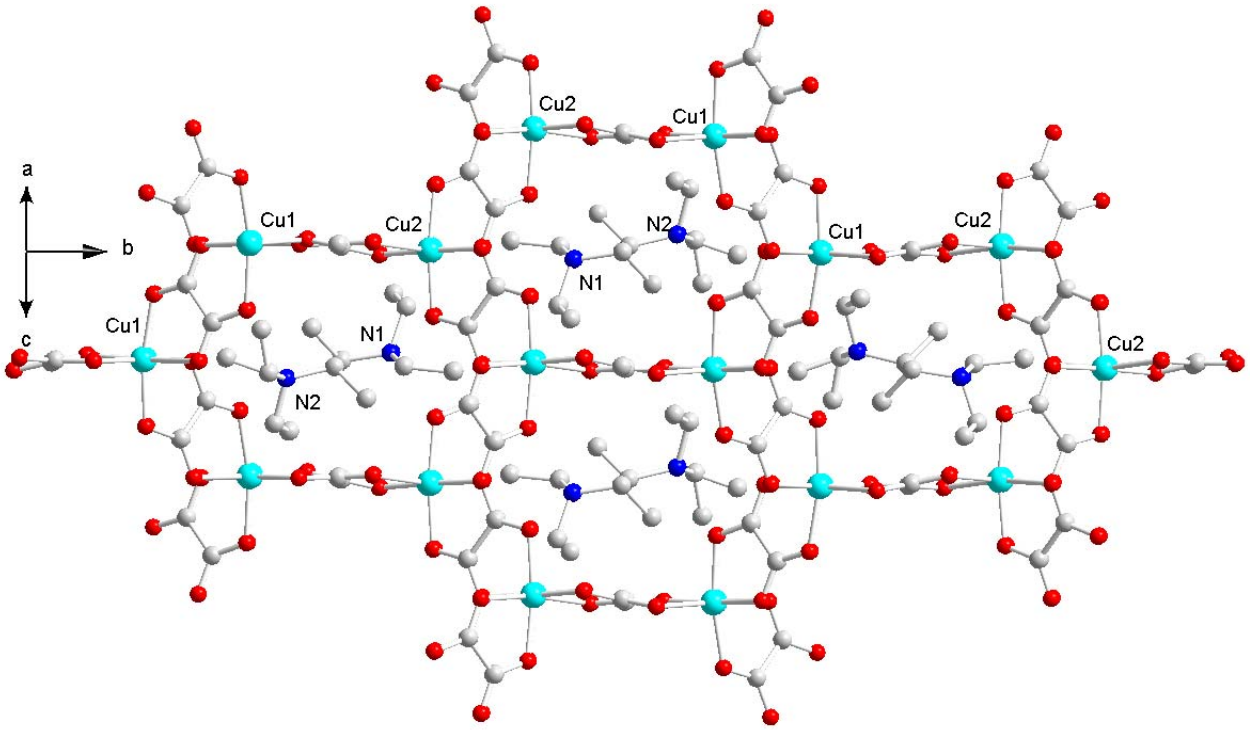


Figure S5. Three-dimensional network of anion $[Cu_2(C_2O_4)_3^{2-}]_n$ viewed along [101] at 135 K. H atoms were omitted for clarity. Colour code: Cu blue, C grey, O red, N, blue.

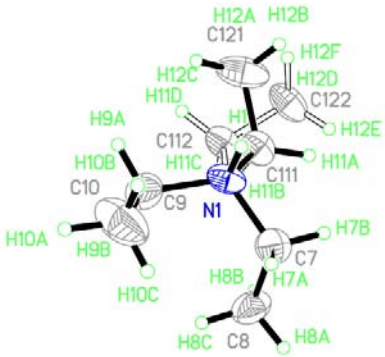
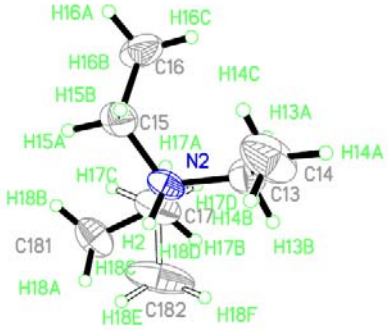
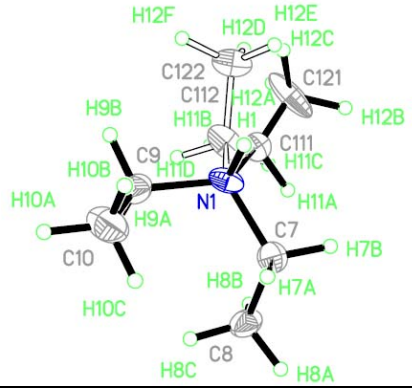
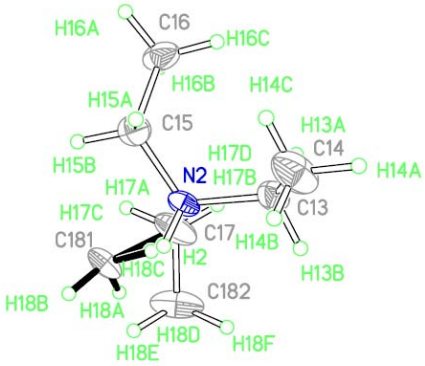
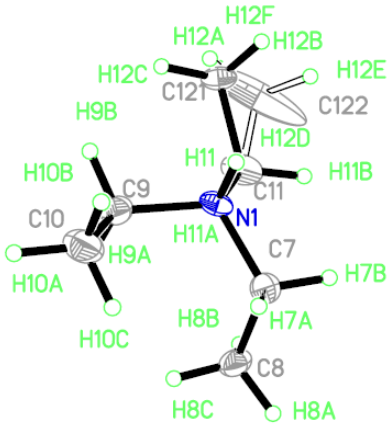
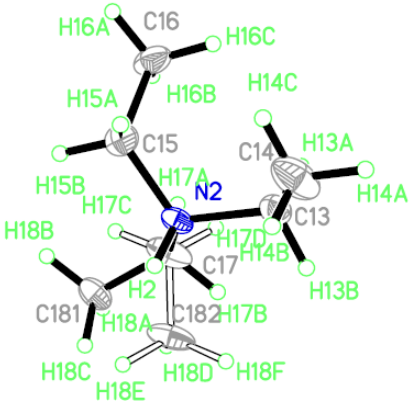
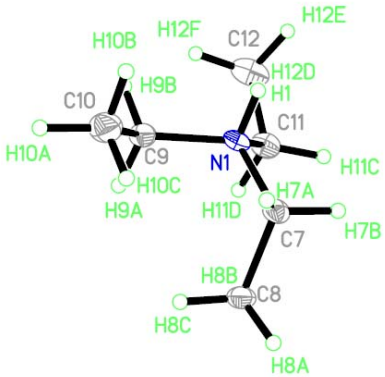
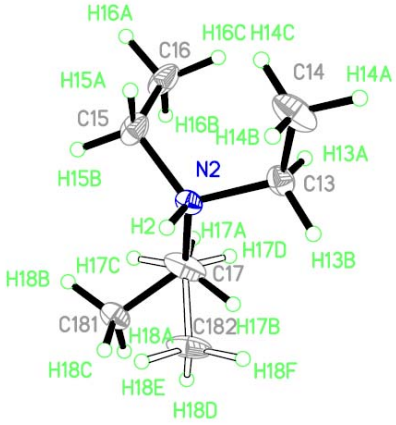
 		293 K
 		180 K
 		155 K
 		135 K

Figure S6. Cations with labels at different temperatures.

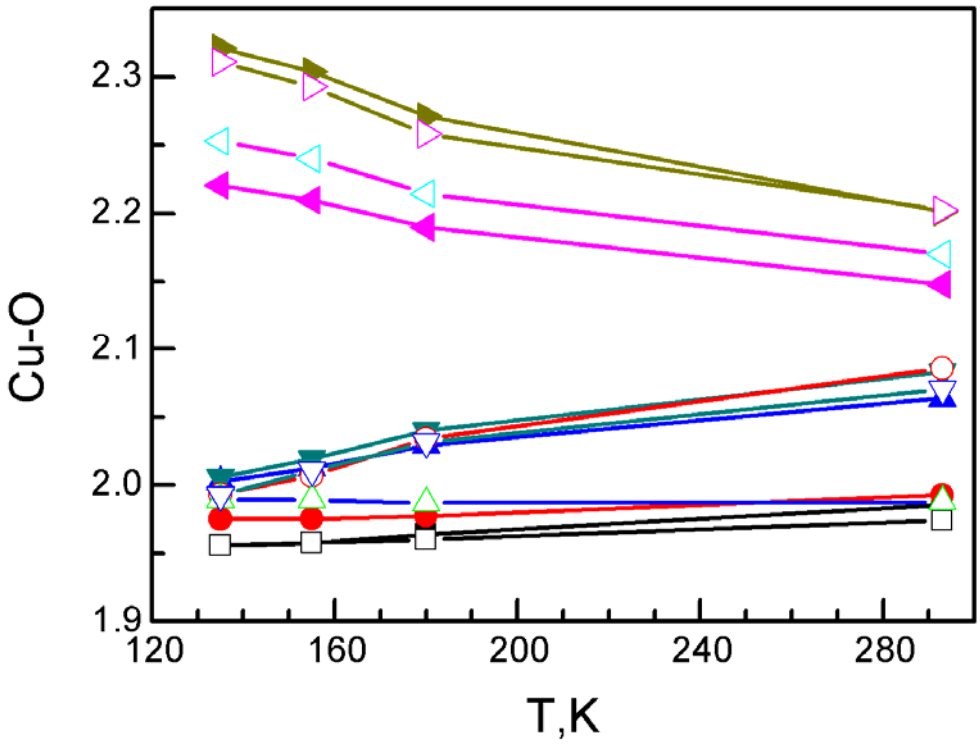


Figure S7. Temperature-dependent Cu−O bond distance in **1** (Cu1, solid; Cu2, empty). Top two are Cu−O distances on axial direction, bottom four are Cu−O distances in the equatorial plane.

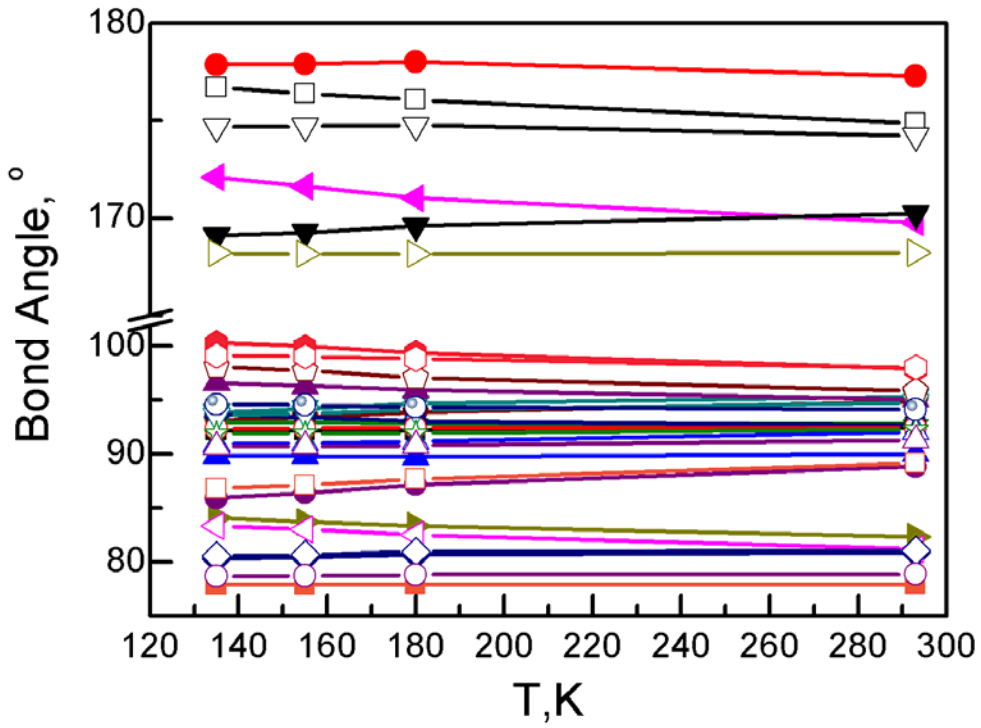


Figure S8. Temperature-dependent O−Cu−O angles in **1** (Cu1, solid; Cu2, empty).

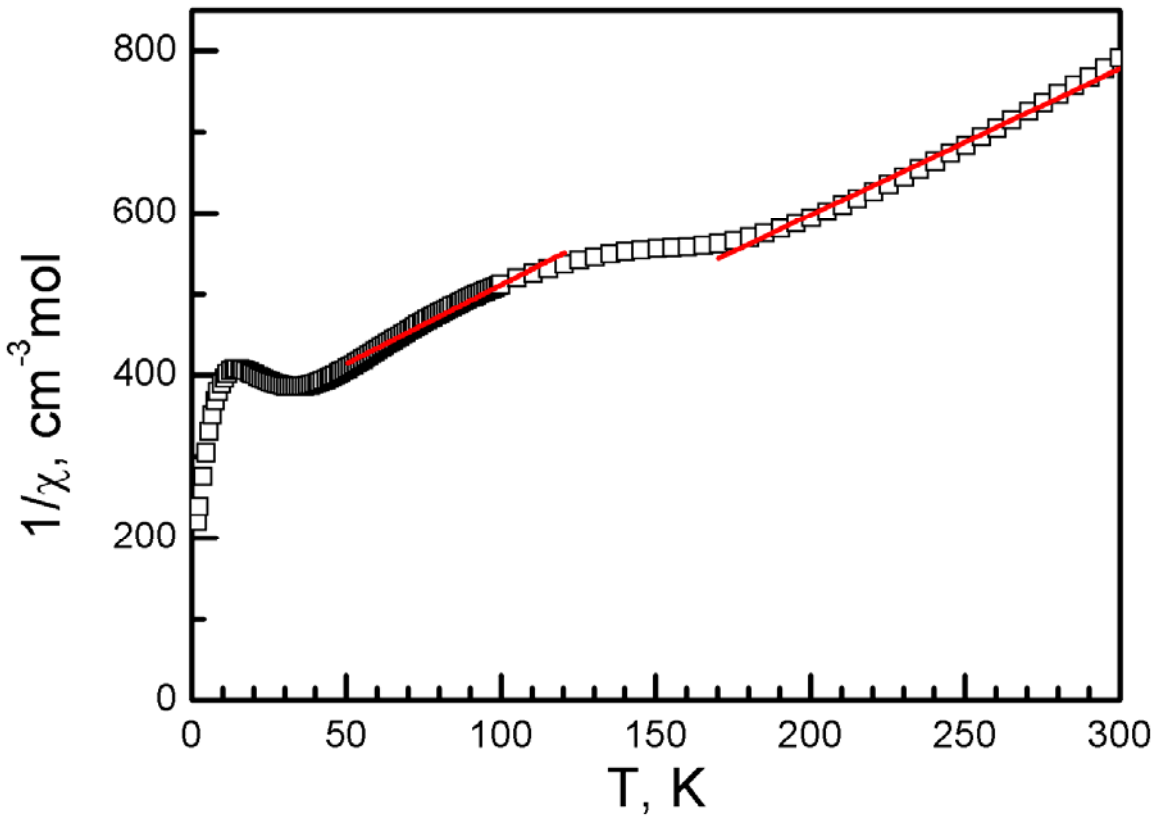


Figure S9. 1/χ-vs-T (black square) plot and Curie-Weiss fitting(red solid) between 50-120K, and 170K~300K.