

Application of Temperature-Controlled Chiral Hybrid Structures Constructed From Copper(II)-Monosubstituted Keggin Polyoxoanions and Copper(II)-Organoamine Complexes in Enantioselective Sensing of Tartaric Acid

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1. Crystal Structures

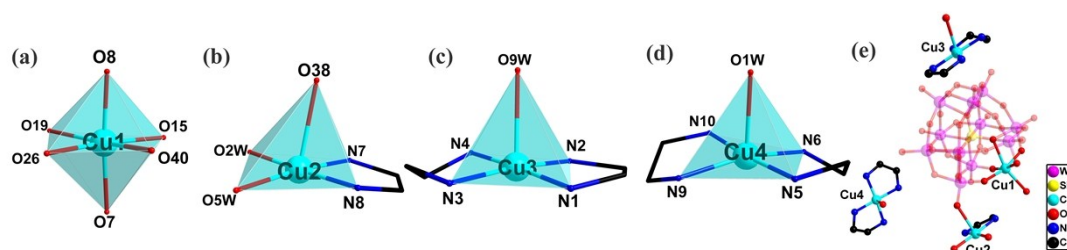


Fig. S1 (a-d) The coordination mode of Cu1, Cu 2, Cu 3, Cu4. (e) The ball-and-stick representation of L-1. For clarity, H atoms and water molecules are omitted.

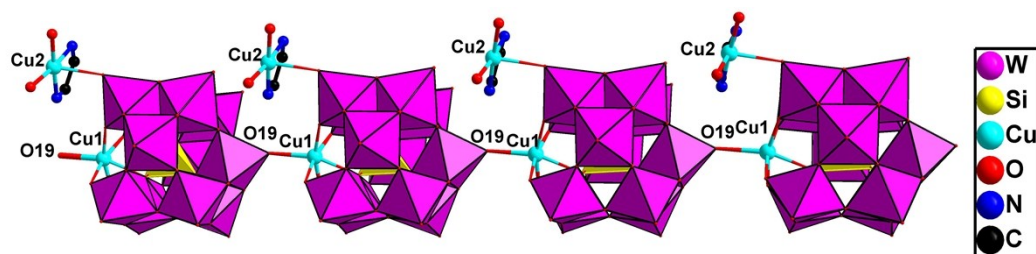


Fig. S2 Ball-stick and polyhedron view of the 1D left-handed chain in L-1.

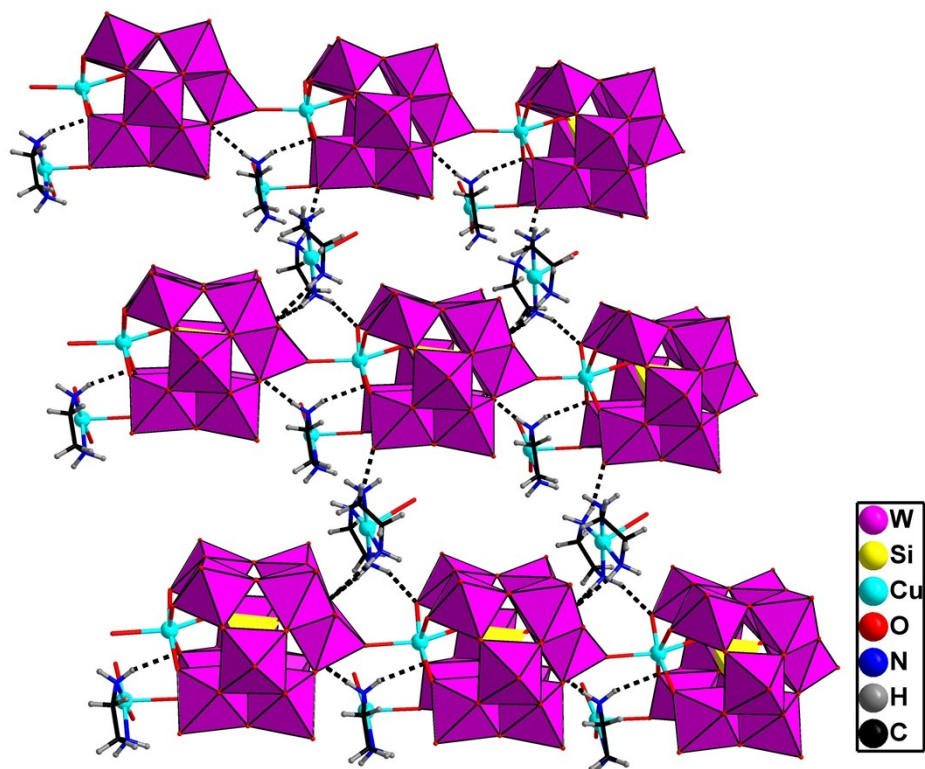


Fig. S3 View of 2D supramolecular chiral sheet in **L-1**, showing the hydrogen-bonding interactions ($\text{N-H}\cdots\text{O}$) between the terminal oxygen atoms of polyoxoanions and organic molecules.

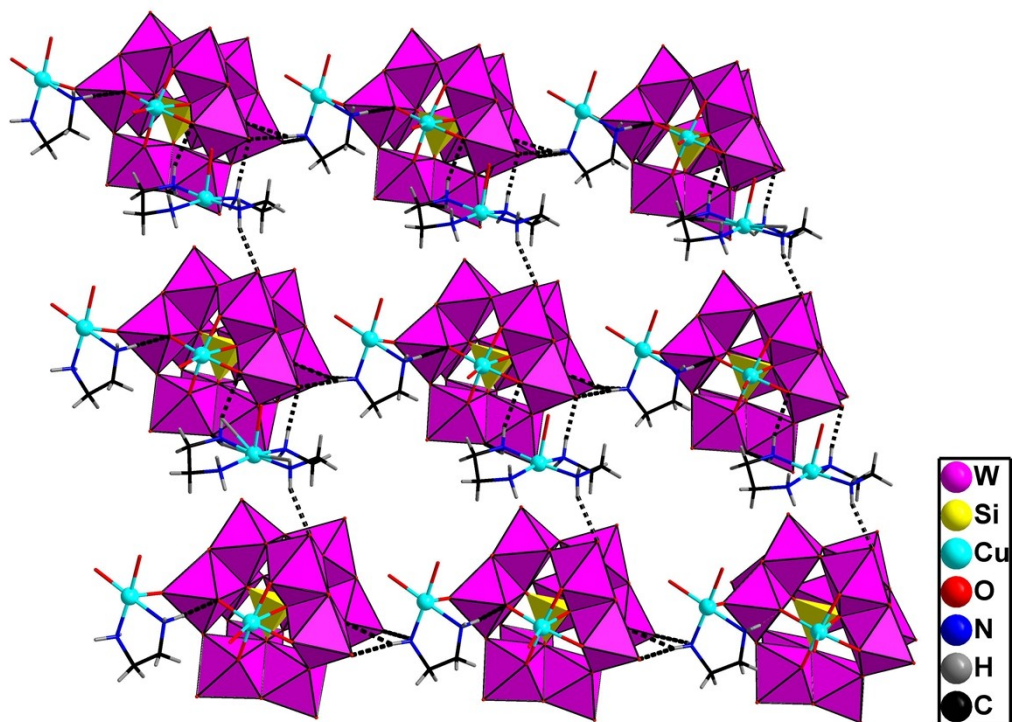


Fig. S4 View of 3D supramolecular chiral framework in **L-1**, showing the hydrogen-

bonding interactions (N-H \cdots O) between the terminal oxygen atoms of polyoxoanions and organic molecules.

2. IR

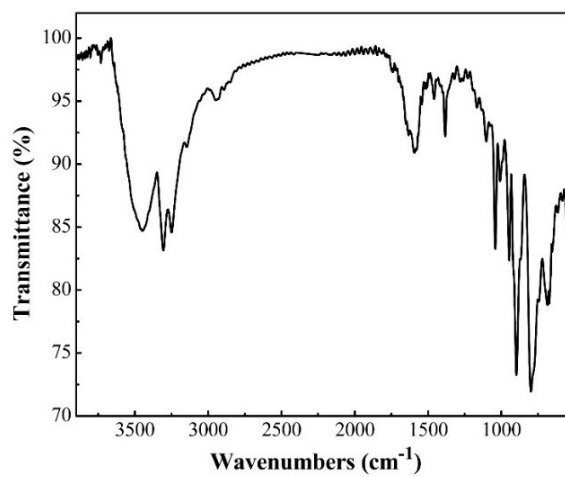


Fig. S5 The IR spectrum of compound 1.

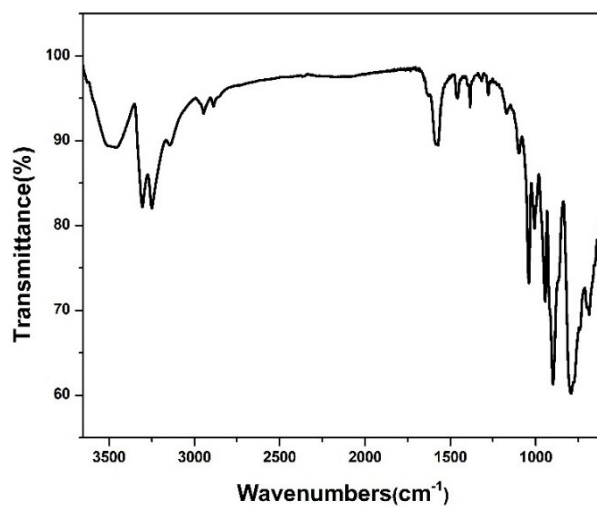


Fig. S6 The IR spectrum of compound 2.

3. TG

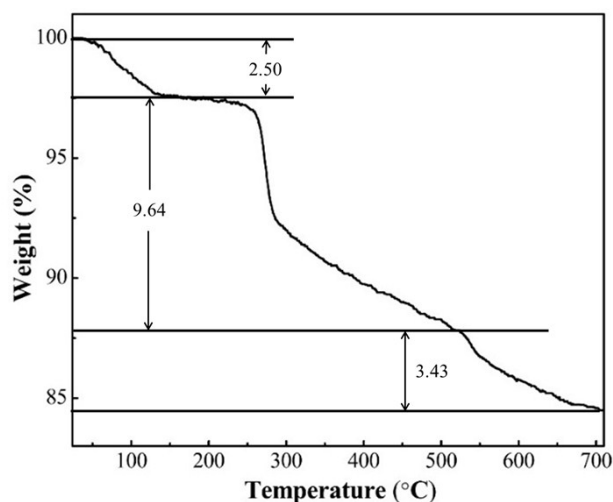


Fig. S7 TGA curve of compound **1**.

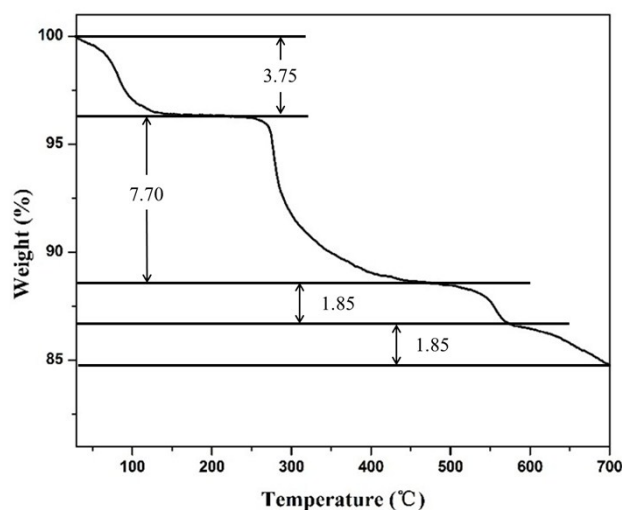


Fig. S8 TGA curve of compound **2**.

TG analysis. The TG curve of compound **1** is shown in Fig, S7. The first weight loss 2.50 % (calc. 2.65 %) occurred in the range of 25 – 170 °C is associated with the remove of 5 lattice H₂O. In the range of 170 – 520 °C, 4 organic ligands ethylenediamine and 4 coordinated H₂O are decomposed with the loss of 9.64 % (calc. 9.20 %). In the range of 520 – 700 °C, the weight loss 3.43 % is attributed to the loss of 1 organic ligand ethylenediamine and the thermal decomposition of the main structure.

Thermal analysis of **2** can be viewed in Fig S8. The first weight loss 3.75 % (calc. 3.67 %) occurred in the range of 25 – 230 °C indicates the release of 2.5 lattice H₂O,

1 coordinated H₂O and 1 organic ligand ethylenediamine. In the range of 230 – 480 °C, 4 organic ligands ethylenediamine are decomposed with the loss of 7.70 % (calc. 7.16 %). In the range of 480 – 570 °C, 1 organic ligands ethylenediamine is decomposed with the loss of 1.85 % (calc. 1.79 %). In the range of 570 – 700 °C, the weight loss 1.85 % is attributed to the thermal decomposition of the main structure. Assuming that the difference corresponds to the moist crystals exposed to air.

4. XRD

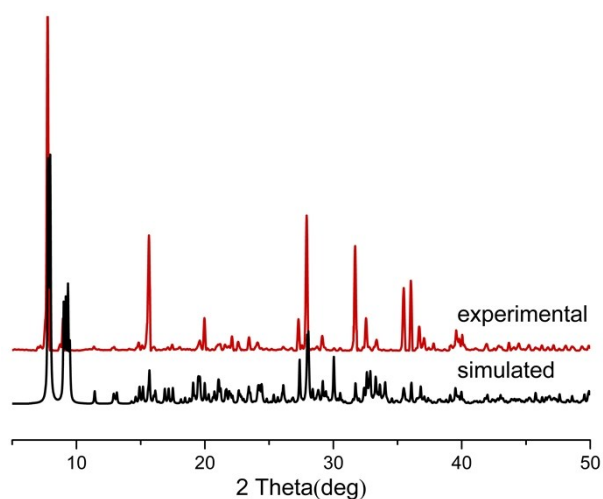


Fig. S9 The XRD patterns of compound **1** under different conditions, Simulated (black), experimental (red).

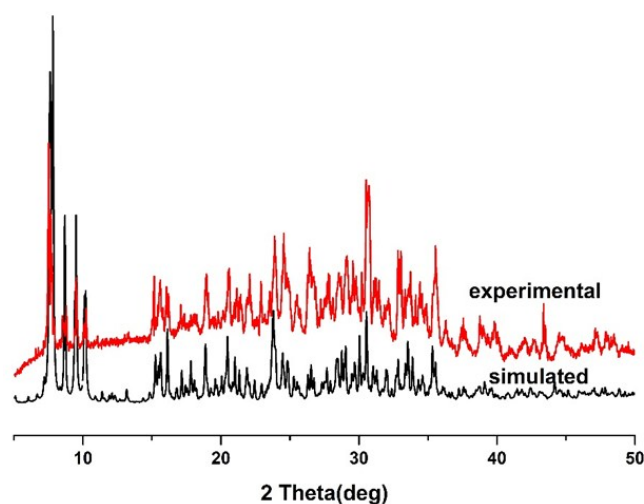


Fig. S10 The XRD patterns of compound **2** under different conditions, Simulated (black), experimental (red).

5. Nonlinear Optical properties

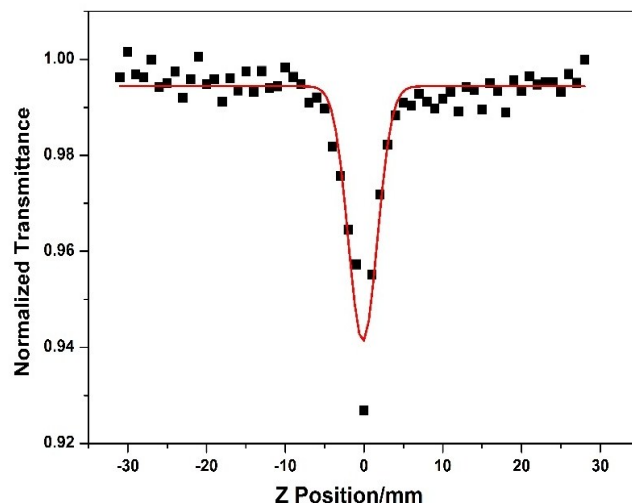


Fig S11 The open aperture Z-scan data of **D-1**. The dots are the experimental data and the solid curve represents the theoretical data, which is modified by the equations (1), (2), (3).

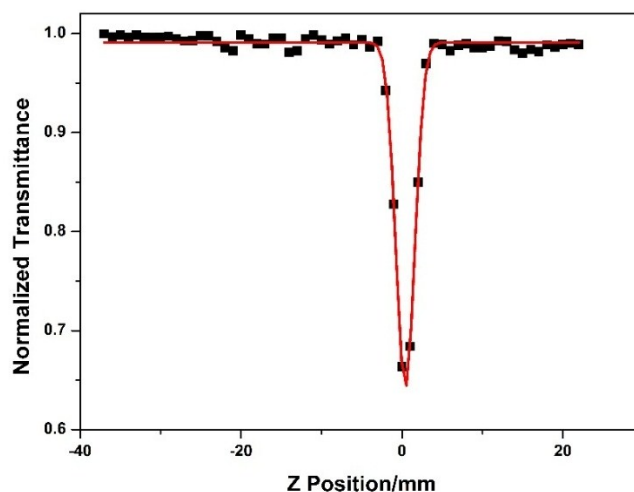


Fig S12. The Z-scan data for **L-1** in water, obtained under an open aperture configuration.

Nonlinear Optical Measurement. Third-order NLO properties of **D-1** and **L-1** are investigated by the open-aperture Z-scan in dimethyl formamide at a concentration of 1.0×10^{-3} mol/L for **D-1** (1.0×10^{-3} mol/L for **L-1**). Chameleon II femtosecond laser pulse and Ti : 95 sapphire systems (740 nm, 80 Hz, 140 fs) were applied to measure third-order nonlinear optics (NLO) properties. Two-photon absorption (TPA) values of **D-1** and **L-1** were measured by the open-aperture Z-scan technique.¹ The nonlinear

absorption coefficient β and the molecular 2PA cross section σ can be determined by equations (1), (2), (3)²:

$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \quad \text{for } |q_0| < 1 \quad (1)$$

$$q_0(z) = \frac{\beta I_0 L_{eff}}{1 + x^2} \quad (2)$$

Where $x = z/z_0$, $z_0 = \pi\omega_0^2/\lambda$ is the diffraction length of the beam, where ω_0 is the spot size at the focus, λ is the wavelength of the beam, and z is the sample position. I_0 is the input intensity at the focus $z = 0$ and equals the input energy divided by $\pi\omega_0^2$, $L_{eff} = (1 - e^{-\alpha L})/\alpha$ is the effective length, in which α is the linear absorption coefficient and L is the sample length. By using the above equations, we obtain the nonlinear absorption coefficient β . Furthermore, the molecular 2PA cross section σ can be determined by the following relationship:

$$\sigma = h\nu\beta/N_A d \times 10^{-3} \quad (3)$$

Here, h is the Planck's constant, ν is the frequency of input intensity, N_A is the Avogadro's constant, and d is the concentration of the compound.

Table S1. Bond valence sum for compound **D-1** and **L-1**.

compound D-1	calculated	compound L-1	calculated
Cu ₁	1.997	Cu ₁	1.960
Cu ₂	1.759	Cu ₂	1.738
Cu ₃	1.957	Cu ₃	1.980
Cu ₄	1.770	Cu ₄	1.907

Table S2. Selected Bond Distances (Å) and angles (°) for compound **D-1**.

Cu(1)-O(7)	1.95(2)	Cu(3)-N(2)	1.95(4)
Cu(1)-O(15)	1.97(2)	Cu(3)-N(1)	1.96(3)

Cu(1)-O(26)	1.99(3)	Cu(3)-N(4)	2.00(5)
Cu(1)-O(8)	2.00(3)	Cu(3)-N(3)	2.04(3)
Cu(1)-O(40) ^a	2.40(3)	Cu(4)-N(10)	2.01(3)
Cu(1)-O(19)#1 ^a	2.40(2)	Cu(4)-N(6)	2.04(4)
Cu(2)-N(8)	1.98(4)	Cu(4)-N(9)	2.05(4)
Cu(2)-O(2W)	2.03(3)	Cu(4)-N(5)	2.06(3)
Cu(2)-O(5W)	2.04(4)	Cu(4)-O(1W)	2.34(3)
Cu(2)-N(7)	2.05(4)	O(19)-Cu(1)#2	2.40(2)
Cu(2)-O(38) ^a	2.44(3)		
O(7)-Cu(1)-O(15)	84.8(10)	N(8)-Cu(2)-O(38)	91.3(13)
O(7)-Cu(1)-O(26)	91.2(11)	O(2W)-Cu(2)-O(38)	91.4(13)
O(15)-Cu(1)-O(26)	166.5(11)	O(5W)-Cu(2)-O(38)	105.2(13)
O(7)-Cu(1)-O(8)	167.0(11)	N(7)-Cu(2)-O(38)	85.3(14)
O(15)-Cu(1)-O(8)	92.6(10)	N(2)-Cu(3)-N(1)	82.1(14)
O(26)-Cu(1)-O(8)	88.5(11)	N(2)-Cu(3)-N(4)	96.5(18)
O(7)-Cu(1)-O(40)	92.3(10)	N(1)-Cu(3)-N(4)	176.4(19)
O(15)-Cu(1)-O(40)	92.2(9)	N(2)-Cu(3)-N(3)	178.1(15)
O(26)-Cu(1)-O(40)	75.1(10)	N(1)-Cu(3)-N(3)	97.3(13)
O(8)-Cu(1)-O(40)	75.1(10)	N(4)-Cu(3)-N(3)	84.2(17)
O(7)-Cu(1)-O(19)#1	96.0(9)	N(10)-Cu(4)-N(6)	96.6(13)
O(15)-Cu(1)-O(19)#1	103.7(9)	N(10)-Cu(4)-N(9)	82.0(13)
O(26)-Cu(1)-O(19)#1	89.5(10)	N(6)-Cu(4)-N(9)	166.8(15)
O(8)-Cu(1)-O(19)#1	97.0(10)	N(10)-Cu(4)-N(5)	178.1(15)
O(40)-Cu(1)-O(19)#1	162.7(9)	N(6)-Cu(4)-N(5)	83.6(13)
N(8)-Cu(2)-O(2W)	175.7(18)	N(9)-Cu(4)-N(5)	98.2(14)
N(8)-Cu(2)-O(5W)	94.4(16)	N(10)-Cu(4)-O(1W)	92.6(12)
O(2W)-Cu(2)-O(5W)	81.7(17)	N(6)-Cu(4)-O(1W)	95.5(13)
N(8)-Cu(2)-N(7)	85.2(16)	N(9)-Cu(4)-O(1W)	97.6(13)
O(2W)-Cu(2)-N(7)	98.3(18)	N(5)-Cu(4)-O(1W)	85.5(13)
O(5W)-Cu(2)-N(7)	169.5(17)		

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

^a Due to the axial extension of the Jahn-Teller effect of copper(II) ion, Cu1-O19 is considered as a usual coordination bond in this article.

Table S3. Selected Bond Distances (Å) and angles (°) for compound **L-1**.

Cu(1)-O(26)	1.95(3)	Cu(3)-N(1)	1.96(4)
Cu(1)-O(8)	1.96(3)	Cu(3)-N(4)	1.97(6)
Cu(1)-O(7)	1.97(3)	Cu(3)-N(2)	1.99(5)
Cu(1)-O(15)	1.99(3)	Cu(3)-N(3)	2.06(5)
Cu(1)-O(40) ^a	2.41(3)	Cu(4)-N(10)	1.97(5)
Cu(1)-O(19)#1 ^a	2.44(3)	Cu(4)-N(5)	2.00(4)
Cu(2)-N(8)	2.00(4)	Cu(4)-N(9)	2.04(4)
Cu(2)-N(7)	2.01(4)	Cu(4)-N(6)	2.07(5)
Cu(2)-O(5W)	2.02(6)	Cu(4)-O(1W)	2.33(4)
Cu(2)-O(2W)	2.07(4)	O(19)-Cu(1)#2	2.44(3)
O(26)-Cu(1)-O(8)	86.5(13)	N(7)-Cu(2)-O(2W)	95.4(16)
O(26)-Cu(1)-O(7)	90.1(12)	O(5W)-Cu(2)-O(2W)	85(2)
O(8)-Cu(1)-O(7)	168.7(13)	N(1)-Cu(3)-N(4)	177(2)
O(26)-Cu(1)-O(15)	164.0(12)	N(1)-Cu(3)-N(2)	87.7(19)
O(8)-Cu(1)-O(15)	92.2(12)	N(4)-Cu(3)-N(2)	95(2)
O(7)-Cu(1)-O(15)	88.1(12)	N(1)-Cu(3)-N(3)	89.9(18)
O(26)-Cu(1)-O(40)	73.7(11)	N(4)-Cu(3)-N(3)	88(2)
O(8)-Cu(1)-O(40)	76.0(12)	N(2)-Cu(3)-N(3)	174.1(18)
O(7)-Cu(1)-O(40)	92.8(11)	N(10)-Cu(4)-N(5)	175(2)
O(15)-Cu(1)-O(40)	90.5(10)	N(10)-Cu(4)-N(9)	83.7(19)
O(26)-Cu(1)-O(19)#1	89.0(12)	N(5)-Cu(4)-N(9)	97.6(18)
O(8)-Cu(1)-O(19)#1	96.5(13)	N(10)-Cu(4)-N(6)	95.1(19)
O(7)-Cu(1)-O(19)#1	94.1(12)	N(5)-Cu(4)-N(6)	84.9(19)
O(15)-Cu(1)-O(19)#1	107.0(11)	N(9)-Cu(4)-N(6)	165(2)
O(40)-Cu(1)-O(19)#1	161.4(10)	N(10)-Cu(4)-O(1W)	87.4(18)
N(8)-Cu(2)-N(7)	84.5(16)	N(5)-Cu(4)-O(1W)	87.6(17)
N(8)-Cu(2)-O(5W)	96(2)	N(9)-Cu(4)-O(1W)	98.9(16)
N(7)-Cu(2)-O(5W)	173.0(19)	N(6)-Cu(4)-O(1W)	95.8(16)

N(8)-Cu(2)-O(2W)	178.3(18)
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Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z; #2 x+1,y,z

Table S4. Selected Bond Distances (Å) and angles (°) for compound **2**.

Cu(1)-O(74)	1.88(2)	Cu(6)-N(11)	2.00(3)
Cu(1)-O(49)	1.938(18)	Cu(6)-N(12)	2.03(2)
Cu(1)-O(60)	1.940(17)	Cu(7)-N(16)	2.03(3)
Cu(1)-O(36)	1.955(16)	Cu(7)-N(13)	2.04(3)
Cu(1)-O(19)	1.96(2)	Cu(7)-N(15)	2.06(2)
Cu(1)-O(41)	2.390(18)	Cu(7)-N(14)	2.06(3)
Cu(2)-O(14)	1.948(19)	Cu(7)-O(2W)	2.35(2)
Cu(2)-O(23)	1.953(16)	Cu(8)-N(6)	1.99(3)
Cu(2)-O(78)#1	1.98(2)	Cu(8)-N(8)	2.01(3)
Cu(2)-O(56)	1.986(15)	Cu(8)-N(5)	2.01(3)
Cu(2)-O(57)	1.991(18)	Cu(8)-N(7)	2.04(3)
Cu(2)-O(51)	2.383(18)	Cu(8)-O(59)	2.380(19)
Cu(3)-O(20)	1.899(19)	Cu(9)-N(24)	1.96(3)
Cu(3)-O(71)	1.958(18)	Cu(9)-N(23)	1.98(3)
Cu(3)-O(32)	1.971(19)	Cu(9)-N(21)	2.01(4)
Cu(3)-O(74)	1.97(2)	Cu(9)-N(22)	2.02(2)
Cu(3)-O(77)	2.009(19)	Cu(9)-O(3W)	2.29(2)
Cu(3)-O(5)	2.344(17)	Cu(10)-N(20)	2.01(3)
Cu(4)-O(55)	1.941(19)	Cu(10)-N(19)	2.02(3)
Cu(4)-O(7)	1.947(18)	Cu(10)-N(18)	2.04(3)
Cu(4)-O(44)	1.947(19)	Cu(10)-N(17)	2.07(4)
Cu(4)-O(45)	1.970(16)	Cu(5)-N(3)	1.96(2)
Cu(4)-O(78)	2.10(2)	Cu(5)-N(4)	2.01(2)
Cu(4)-O(37)	2.403(18)	Cu(5)-N(2)	2.02(2)
Cu(6)-N(9)	2.00(3)	Cu(5)-N(1)	2.02(2)
Cu(6)-N(10)	2.00(3)	Cu(5)-O(39)	2.418(19)

O(74)-Cu(1)-O(49)	100.3(8)	O(7)-Cu(4)-O(37)	73.2(6)
O(74)-Cu(1)-O(60)	99.2(8)	O(44)-Cu(4)-O(37)	73.8(7)
O(49)-Cu(1)-O(60)	89.4(7)	O(45)-Cu(4)-O(37)	88.9(6)
O(74)-Cu(1)-O(36)	99.9(8)	O(78)-Cu(4)-O(37)	168.8(7)
O(49)-Cu(1)-O(36)	159.7(7)	N(9)-Cu(6)-N(10)	83.5(11)
O(60)-Cu(1)-O(36)	89.6(7)	N(9)-Cu(6)-N(11)	173.6(11)
O(74)-Cu(1)-O(19)	98.1(8)	N(10)-Cu(6)-N(11)	95.5(11)
O(49)-Cu(1)-O(19)	84.9(8)	N(9)-Cu(6)-N(12)	97.4(10)
O(60)-Cu(1)-O(19)	162.5(7)	N(10)-Cu(6)-N(12)	168.7(10)
O(36)-Cu(1)-O(19)	90.1(8)	N(11)-Cu(6)-N(12)	84.8(10)
O(74)-Cu(1)-O(41)	169.7(8)	N(16)-Cu(7)-N(13)	173.7(12)
O(49)-Cu(1)-O(41)	87.1(7)	N(16)-Cu(7)-N(15)	82.8(11)
O(60)-Cu(1)-O(41)	73.4(6)	N(13)-Cu(7)-N(15)	97.0(11)
O(36)-Cu(1)-O(41)	73.2(6)	N(16)-Cu(7)-N(14)	94.7(12)
O(19)-Cu(1)-O(41)	89.8(7)	N(13)-Cu(7)-N(14)	84.0(11)
O(14)-Cu(2)-O(23)	85.2(7)	N(15)-Cu(7)-N(14)	165.9(12)
O(14)-Cu(2)-O(78)#1	101.7(8)	N(16)-Cu(7)-O(2W)	98.8(11)
O(23)-Cu(2)-O(78)#1	104.0(8)	N(13)-Cu(7)-O(2W)	87.5(10)
O(14)-Cu(2)-O(56)	161.1(7)	N(15)-Cu(7)-O(2W)	98.7(9)
O(23)-Cu(2)-O(56)	89.9(7)	N(14)-Cu(7)-O(2W)	95.4(10)
O(78)#1-Cu(2)-O(56)	97.2(8)	N(6)-Cu(8)-N(8)	175.1(12)
O(14)-Cu(2)-O(57)	91.9(7)	N(6)-Cu(8)-N(5)	82.5(11)
O(23)-Cu(2)-O(57)	160.1(7)	N(8)-Cu(8)-N(5)	96.0(11)
O(78)#1-Cu(2)-O(57)	95.9(8)	N(6)-Cu(8)-N(7)	97.9(10)
O(56)-Cu(2)-O(57)	86.5(7)	N(8)-Cu(8)-N(7)	83.3(9)
O(14)-Cu(2)-O(51)	87.4(7)	N(5)-Cu(8)-N(7)	175.3(12)
O(23)-Cu(2)-O(51)	86.0(6)	N(6)-Cu(8)-O(59)	84.3(9)
O(78)#1-Cu(2)-O(51)	166.9(7)	N(8)-Cu(8)-O(59)	100.1(9)
O(56)-Cu(2)-O(51)	74.0(6)	N(5)-Cu(8)-O(59)	81.5(10)
O(57)-Cu(2)-O(51)	74.2(6)	N(7)-Cu(8)-O(59)	103.2(9)

O(20)-Cu(3)-O(71)	162.9(8)	N(24)-Cu(9)-N(23)	84.4(12)
O(20)-Cu(3)-O(32)	87.2(7)	N(24)-Cu(9)-N(21)	97.8(14)
O(71)-Cu(3)-O(32)	90.8(8)	N(23)-Cu(9)-N(21)	176.4(13)
O(20)-Cu(3)-O(74)	97.2(8)	N(24)-Cu(9)-N(22)	172.0(13)
O(71)-Cu(3)-O(74)	100.0(8)	N(23)-Cu(9)-N(22)	95.8(10)
O(32)-Cu(3)-O(74)	97.2(8)	N(21)-Cu(9)-N(22)	81.6(13)
O(20)-Cu(3)-O(77)	90.4(8)	N(24)-Cu(9)-O(3W)	90.6(12)
O(71)-Cu(3)-O(77)	87.7(8)	N(23)-Cu(9)-O(3W)	90.6(11)
O(32)-Cu(3)-O(77)	166.5(8)	N(21)-Cu(9)-O(3W)	92.3(13)
O(74)-Cu(3)-O(77)	96.3(9)	N(22)-Cu(9)-O(3W)	97.4(10)
O(20)-Cu(3)-O(5)	87.2(7)	N(20)-Cu(10)-N(19)	83.0(12)
O(71)-Cu(3)-O(5)	75.8(7)	N(20)-Cu(10)-N(18)	95.3(13)
O(32)-Cu(3)-O(5)	89.8(7)	N(19)-Cu(10)-N(18)	176.3(13)
O(74)-Cu(3)-O(5)	171.9(8)	N(20)-Cu(10)-N(17)	178.2(14)
O(77)-Cu(3)-O(5)	76.8(7)	N(19)-Cu(10)-N(17)	95.3(15)
O(55)-Cu(4)-O(7)	90.5(8)	N(18)-Cu(10)-N(17)	86.4(15)
O(55)-Cu(4)-O(44)	160.7(7)	N(3)-Cu(5)-N(4)	83.1(8)
O(7)-Cu(4)-O(44)	89.5(8)	N(3)-Cu(5)-N(2)	97.4(9)
O(55)-Cu(4)-O(45)	85.0(7)	N(4)-Cu(5)-N(2)	178.0(10)
O(7)-Cu(4)-O(45)	161.8(7)	N(3)-Cu(5)-N(1)	164.9(10)
O(44)-Cu(4)-O(45)	89.0(7)	N(4)-Cu(5)-N(1)	94.9(9)
O(55)-Cu(4)-O(78)	96.4(8)	N(2)-Cu(5)-N(1)	85.2(9)
O(7)-Cu(4)-O(78)	96.3(8)	N(3)-Cu(5)-O(39)	111.3(9)
O(44)-Cu(4)-O(78)	102.7(8)	N(4)-Cu(5)-O(39)	98.4(8)
O(45)-Cu(4)-O(78)	101.7(8)	N(2)-Cu(5)-O(39)	79.6(8)
O(55)-Cu(4)-O(37)	87.7(7)	N(1)-Cu(5)-O(39)	83.8(8)

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

Table S5. Distances and angles [Å, °] of hydrogen bonds for compound **D-1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠D–H···A
N5 -- H5C···O23	0.89	2.2	3.00(5)	149
N7 -- H7D···O36	0.89	2.17	2.99(6)	153
N8 -- H8D···O15	0.89	2.21	3.06(5)	159
N10 -- H10D···O7	0.89	2.46	3.06(4)	124
N10 -- H10D···O26	0.89	2.25	3.09(5)	158

Table S6. Distances and angles [Å, °] of hydrogen bonds for compound **L-1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠D–H···A
N1-- H1C···O8	0.89	2.12	2.92(6)	149
N1-- H1D···O10	0.89	2.27	3.07(6)	149
N2-- H2D···O5	0.89	2.13	2.94(6)	152
N3-- H3C···O10	0.89	2.46	3.20(6)	141
N5-- H5D···O23	0.89	2.17	3.01(7)	158
N6-- H6D···O36	0.89	2	2.86(6)	163
N7-- H7C···O36	0.89	2.15	3.00(5)	160
N7-- H7C···O37	0.89	2.55	3.18(4)	128
N7-- H7D···O30	0.89	2.47	3.27(6)	149
N8-- H8C···O15	0.89	2.18	3.03(7)	161
N8-- H8D···O12	0.89	2.24	3.08(6)	155
N10-- H10C···O26	0.89	2.2	3.06(7)	162
N10-- H10D···O31	0.89	2.53	3.32(7)	149

Table S7. Distances and angles [Å, °] of hydrogen bonds for compound **2**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠D–H···A
N1 -- H1C···O21	0.89	2.26	3.07(3)	151
N2 -- H2D···O3	0.89	2.5	3.23(3)	140

N3 -- H3C···O3	0.89	2.5	3.17(3)	132
N3 -- H3C···O76	0.89	2.39	3.22(3)	154
N3 -- H3D···O48	0.89	2.6	3.17(3)	123
N4 -- H4C···O49	0.89	2.31	3.08(3)	145
N4 -- H4C···O74	0.89	2.5	3.21(3)	136
N4 -- H4D···O21	0.89	2.15	2.98(3)	154
N6 -- H6B···O68	0.89	2.11	2.96(3)	159
N7 -- H7C···O18	0.89	2.54	3.38(3)	158
N7 -- H7C···O68	0.89	2.48	3.18(3)	135
N7 -- H7D···O26	0.89	2.36	3.03(3)	132
N8 -- H8C···O23	0.89	2.5	3.24(3)	141
N8 -- H8D···O52	0.89	2.11	2.98(4)	166
N9 -- H9C···O22	0.89	2.47	3.30(3)	155
N9 -- H9C···O61	0.89	2.59	3.27(3)	134
N10 -- H10C···O35	0.89	2.15	2.95(3)	148
N10 -- H10D···O4	0.89	2.13	3.00(3)	166
N11 -- H11C···O77	0.89	2.34	3.17(4)	156
N11 -- H11D···O19	0.89	2.51	3.23(3)	139
N11 -- H11D···O36	0.89	2.26	3.06(3)	149
N12 -- H12C···O54	0.89	2.31	3.17(3)	163
N12 -- H12D···O8	0.89	2.08	2.87(3)	148
N13 -- H13D···O67	0.89	2.3	3.17(3)	166
N14 -- H14C···O65	0.89	2.29	3.16(4)	164
N14 -- H14D···O73	0.89	2.52	3.38(4)	162
N15 -- H15C···O76	0.89	2.38	3.24(3)	163
N15 -- H15D···O21	0.89	2.6	3.25(3)	131
N18 -- H18C···O17	0.89	2.33	3.19(4)	164
N19 -- H19C···O60	0.89	2.26	3.10(4)	158
N19 -- H19D···O32	0.89	2.42	3.24(4)	153

N20 -- H20D···O72	0.89	2.14	2.97(3)	156
N21 -- H21C···O61	0.89	2.1	2.91(4)	152
N21 -- H21D···O25	0.89	2.21	3.08(4)	165
N22 -- H22C···O33	0.89	1.94	2.82(3)	166
N22 -- H22D···O13	0.89	2.06	2.94(3)	170
N23 -- H23C···O53	0.89	2.35	3.20(3)	160
N23 -- H23D···O16	0.89	2.18	2.93(3)	142
N24 -- H24C···O61	0.89	2.33	3.18(4)	161
N24 -- H24D···O25	0.89	2.41	3.29(4)	170

- (a) N. L. Toh, M. Nagarathinam and J. J. Vittal, *Angew. Chem. Int. Ed.*, 2005, **44**, 2237-2241; (b) C. Hu and U. Englert, *Angew. Chem. Int. Ed.*, 2005, **44**, 2281-2283; (c) T. Tahier and C. L. Oliver, *CrystEngComm*, 2017, **19**, 3607-3618; (d) D. K. Kumar, D. A. Jose, A. Das and P. Dastidar, *Inorg. Chem.*, 2005, **44**, 6933-6935.
- (a) M. C. Bernini, F. Gandara, M. Iglesias, N. Snejko, E. Gutierrez-Puebla, E. V. Brusau, G. E. Narda and M. A. Monge, *Chem. Eur. J.*, 2009, **15**, 4896-4905; (b) P. Cui, L. Ren, Z. Chen, H. Hu, B. Zhao, W. Shi and P. Cheng, *Inorg. Chem.* 2012, **51**, 2303-2310.