Electronic Supplementary Material (ESI) for Dalton Transactions.

A Discrete Cu^{II}_6 Cluster and a 3D Mn^{II}-Cu^{II} Framework Based on Assembly of Mn_2Cu_4 Clusters: Synthesis, Structure and Magnetic Properties

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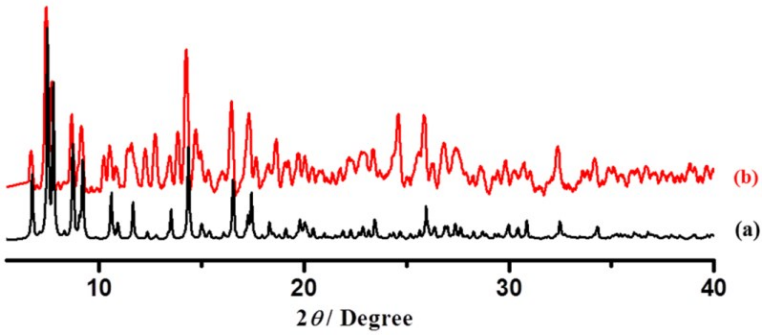

Fig. S1. PXRD patterns of compound **1**: (a) simulated; (b) bulk as-synthesized. Similarity in simulated and as-synthesized pattern indicates high purity of the compound.

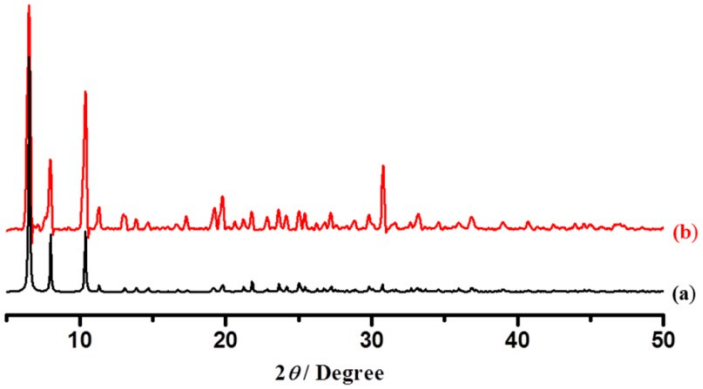

Fig. S2. PXRD patterns of compound **2**: (a) simulated; (b) bulk as-synthesized.

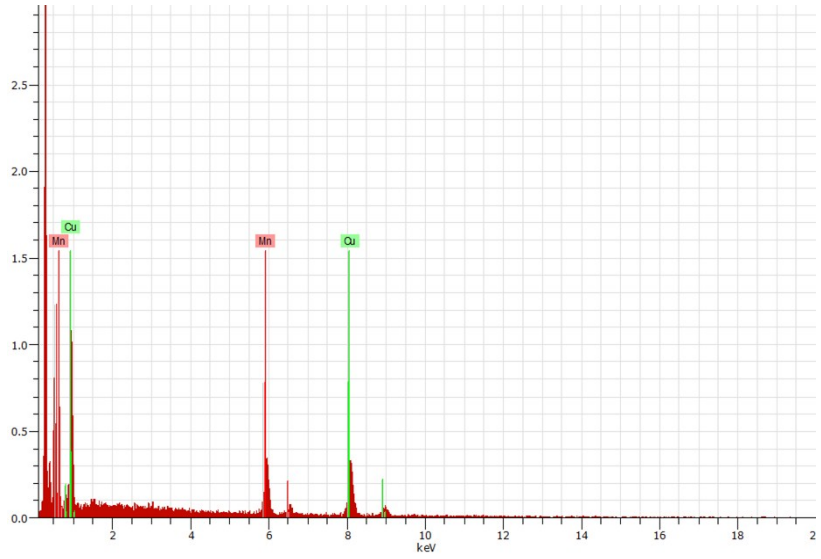

Fig. S3. EDX analysis for **2** confirming the presence of both Cu(II) and Mn(II).

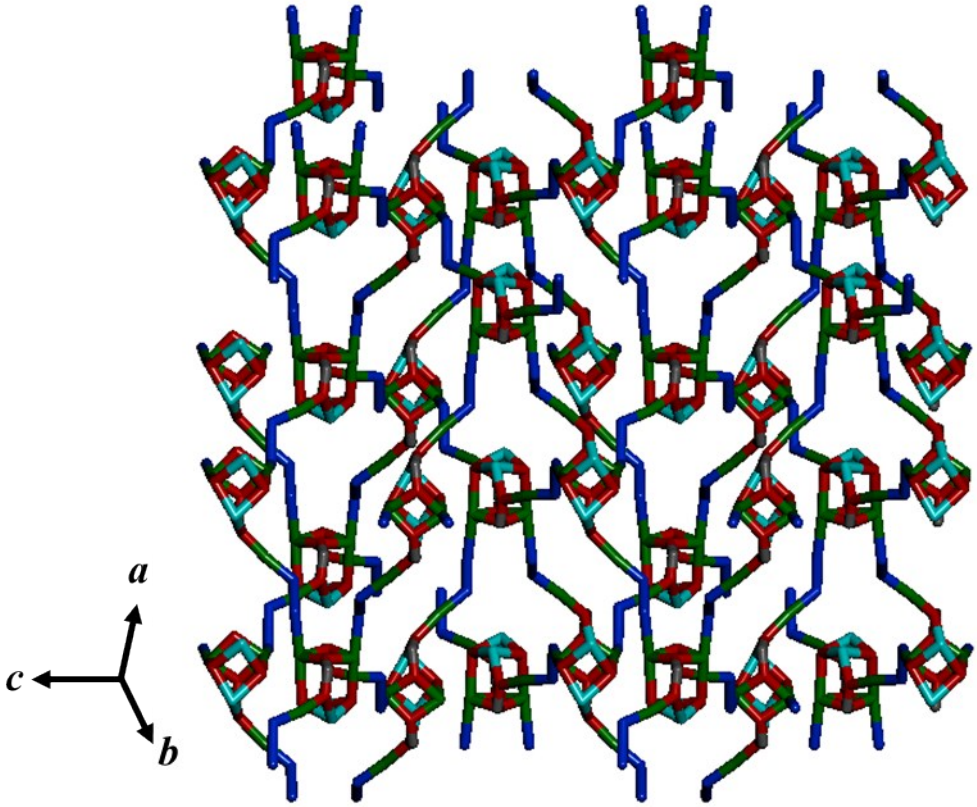

Fig. S4. The simplified 3D net of **2.** Color code: Cu: green; Mn: cyan; C: grey; O: red; N: blue.

Table S1. Crystal data and structure refinement parameters for **1** and **2**

parameters	**1**	**2**
empirical formula	$C_{72}H_{60}Cu_6N_{16}O_{22}$	$C_{33}H_{28}Cu_2MnN_{10}O_{10}$
formula weight	1882.61	906.68
crystal system	triclinic	tetragonal
space group	$P\bar{1}$	$P4_32_12$
a, Å	13.8873(2)	19.165(5)
b, Å	16.1982(3)	19.165(5)
c, Å	17.5410(3)	18.967(5)
α, deg	90.499(1)	90
β, deg	108.881(1)	90
γ, deg	94.530(1)	90
V, Å^3	3719.40(11)	6967(4)
Z	2	8
T, K	298	298
D_{calcd}, g/cm^3	1.676	1.725
F (000)	1896	3656
R_{int}	0.050	0.088
GOF on F^2	0.913	1.039
R_1[a]	0.0399	0.0316
R_w[b]	0.1186	0.0699

[a] $R_1[I>2\sigma(I)] = \sum||F_o|-|F_c||/\sum|F_o|$; [b] R_w[all data] $= [\sum\{w(F_o^2-F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$

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

Cu1-O9	1.929(2)	Cu1-O1	1.947(3)
Cu1-N4	1.973(4)	Cu1-N1	1.962(3)
Cu1-O4	2.423(3)	Cu2-O1	1.947(3)
Cu2-O1W	2.572(4)	Cu2-O3	1.958(3)
Cu2-O14	2.546(4)	Cu2-N2	1.961(4)
Cu2-N6	2.002(3)	Cu3-O1	1.967(3)
Cu3-O2	2.406(5)	Cu3-O8	1.926(3)
Cu3-N3	1.971(3)	Cu3-N15	1.971(4)
Cu3-O6	2.763(4)	Cu4-N9	1.986(3)
Cu4-N12	1.966(4)	Cu4-O7	1.962(3)
Cu4-O12	1.930(3)	Cu4-O15	2.472(5)
Cu4-O19	2.550(3)	Cu5-N11	1.978(4)
Cu5-O16	2.537(5)	Cu5-N10	1.979(3)
Cu5-O20	2.673(4)	Cu5-O7	1.963(3)
Cu5-O11	1.924(3)	Cu6-O7	1.941(3)
Cu6-O2W	2.577(4)	Cu6-O10	1.940(3)
Cu6-N8	1.958(4)	Cu6-N16	1.976(3)
Cu1-Cu2	3.223(7)	Cu1-Cu3	3.191(2)
Cu2-Cu3	3.245(3)		

O1-Cu1-N1	172.01(16)	O2-Cu3-O8	88.96(15)
O2-Cu3-N3	92.99(16)	O2-Cu3-N15	90.40(16)
O2-Cu3-O6	170.98(14)	O8-Cu3-N3	96.58(14)
O4-Cu1-N1	101.72(13)	O8-Cu3-N15	177.10(13)
O4-Cu1-N4	92.09(13)	O6a -Cu3-O8	88.89(12)
N1-Cu1-N4	81.62(15)	N3-Cu3-N15	80.64(15)
O1-Cu2-O1W	90.23(13)	O6a-Cu3-N3	78.56(13)
O1-Cu2-O3	95.63(12)	O6a-Cu3-N15	91.31(14)
O1-Cu2-O14	88.06(13)	O15-Cu4-N12	88.47(16)
O1-Cu2-N2	165.27(13)	O19-Cu4-N9	99.00(13)
O1-Cu2-N6	88.45(14)	O19-Cu4-N12	89.83(13)
O1W-Cu2-O3	79.42(12)	N9-Cu4-N12	81.11(15)
O1W-Cu2-O14	163.02(13)	O7-Cu4-N12	90.26(13)
O1W-Cu2-N2	84.76(14)	O10-Cu4-O12	159.91(10)
O1W-Cu2-N6	114.01(13)	O10-Cu4-O15	91.90(13)
O3-Cu2-O14	83.94(14)	O10-Cu4-O19	85.60(9)
O3-Cu2-N2	97.05(13)	O10-Cu4-N9	103.56(13)
O3-Cu2-N6	166.01(14)	O14-Cu2-N2	100.70(14)
O12-Cu4-O15	89.25(14)	O14-Cu2-N6	82.83(15)
O12-Cu4-O19	92.55(12)	N2-Cu2-N6	81.01(15)
O12-Cu4-N9	96.49(14)	O1-Cu3-O2	99.05(14)
O12-Cu4-N12	176.87(14)	O1-Cu3-O8	93.58(12)
O7-Cu4-O10	67.80(10)	O1-Cu3-N3	164.38(15)
O7-Cu4-O12	92.22(12)	O7-Cu4-O15	99.13(12)
N8-Cu6-N16	80.99(15)	O7-Cu4-O19	78.41(11)
O7-Cu4-N9	171.03(14)	O7-Cu6-O11	67.96(10)
O15-Cu4-O19	177.01(12)	O7-Cu6-O16	70.55(12)
O15-Cu4-N9	83.17(14)	O7-Cu6-N8	170.35(13)
O7-Cu5-O16	80.44(14)	O7-Cu6-N16	90.24(14)
O7-Cu5-O11	94.09(12)	O10-Cu6-O11	155.27(11)
O7-Cu5-O12	66.52(10)	O10-Cu6-O16	98.53(13)
O7-Cu5-O20a	88.38(11)	O10-Cu6-N8	95.56(14)
O11-Cu5-O12	160.59(11)	O10-Cu6-N16	165.32(15)
O11-Cu5-O16	81.69(14)	O11-Cu6-O16	60.34(11)
O11-Cu5-N10	95.69(13)	O11-Cu6-N8	103.44(11)
O11-Cu5-N11	174.85(15)	O2W-Cu6-O7	87.93(12)
O7-Cu5-N10	165.79(15)	O2W-Cu6-O10	77.79(12)
O7-Cu5-N11	88.80(13)	O2W-Cu6-O11	116.51(11)
O12-Cu5-O16	95.05(13)	O2W-Cu6-O16	157.98(13)
O12-Cu5-N10	103.28(12)	O2W-Cu6-N8	92.40(14)
O12-Cu5-N11	22.56(11)	O2W-Cu6-N16	116.47(14)
O12-Cu5-O20	90.09(9)	O7-Cu6-O10	93.94(12)
O16-Cu5-N10	111.17(17)	Cu1-O1-Cu2	111.71(14)
O16-Cu5-N11	103.02(16)	Cu1-O1-Cu3	109.23(14)
O16-Cu5-O20	164.61(14)	Cu2-O1-Cu3	111.99(14)
N10-Cu5-N11	80.73(14)	O20a-Cu5-N10	81.57(14)

O11-Cu6-N16	22.51(12)	O16-Cu6-N16	69.63(14)
Cu4-O7-Cu5	107.05(13)	Cu4-O7-Cu6	112.46(14)
Cu5-O7-Cu6	110.02(13)	Cu1-Cu2-Cu3	59.12(11)
Cu1-Cu3-Cu2	60.11(11)	Cu2-Cu1-Cu3	60.77(7)

Table S3. Selected bond distances (Å) and bond angles (°) for **2**

Cu1-O1	1.930(4)	Cu1-O3	2.523(4)
Cu1-N1	1.998(6)	Cu1-N3	1.981(6)
Cu1-N9	2.595(8)	Cu1-O1	1.953(4)
Cu2-O2	1.913(5)	Cu2-O5	2.071(6)
Cu2-N2	2.020(6)	Cu2-N6	2.248(6)
Cu2-N7	1.972(8)	Mn1-O2	2.074(4)
Mn1-O3	2.167(4)	Mn1-O5	2.334(5)
Mn1-N4	2.311(6)	Mn1-N5	2.253(6)
Mn1-O3a	2.180(4)		
O1-Cu1-O3	98.22(15)	O2-Mn1-N5	136.14(19)
O1-Cu1-N1	81.0(2)	O2-Mn1-O3a	94.24(17)
O1-Cu1-N3	173.4(2)	O3-Mn1-O5	164.31(18)
O3-Mn1-N4	71.26(18)	O1-Cu1-O1a	79.80(16)
O3-Mn1-N5	105.45(18)	O3-Cu1-N1	105.03(19)
O3-Mn1-O3a	77.08(15)	O3-Cu1-N3	75.18(19)
O5-Mn1-N4	123.01(19)	O5-Cu2-N7	100.2(3)
O3-Cu1-N9a	167.96(19)	O5-Mn1-N5	71.6(2)
O1a-Cu1-O3	88.14(14)	O3a-Mn1-O5	89.66(16)
N1-Cu1-N3	100.7(2)	N4-Mn1-N5	85.7(2)
N1-Cu1-N9a	83.9(2)	O3a-Mn1-N4	146.90(18)
O1a -Cu1-N1	158.1(2)	O3a-Mn1-N5	112.30(18)
N3-Cu1-N9a	95.4(2)	O1a -Cu1-N3	99.5(2)
Cu1-O1-Cu1a	98.91(17)	O1a -Cu1-N9a	86.0(2)
O2-Cu2-O5	84.20(18)	Cu2-O2-Mn1	107.7(2)
O2-Cu2-N2	81.0(2)	O2-Cu2-N6	93.1(2)
O2-Cu2-N7	171.0(3)	Cu1-O3-Mn1	98.72(15)
O5-Cu2-N2	153.3(2)	O5-Cu2-N6	74.2(2)
Cu1-O3-Mn1a	111.67(16)	N2-Cu2-N6	128.6(2)
Mn1-O3-Mn1a	95.92(15)	N2-Cu2-N7	91.9(3)
N6-Cu2-N7	95.7(3)	Cu2-O5-Mn	93.73(19)
O2-Mn1-O3	114.43(16)	O2-Mn1-O5	74.41(19)

Symmetry code: a = y, x, -z