

Electronic Supplementary Information (ESI)

***In situ* syntheses, crystal structures and magnetic properties of Cu^{II} and Mn^{II} coordination assemblies based on a novel heteroalicyclic dicarboxylate tecton and N-donor co-ligands[†]**

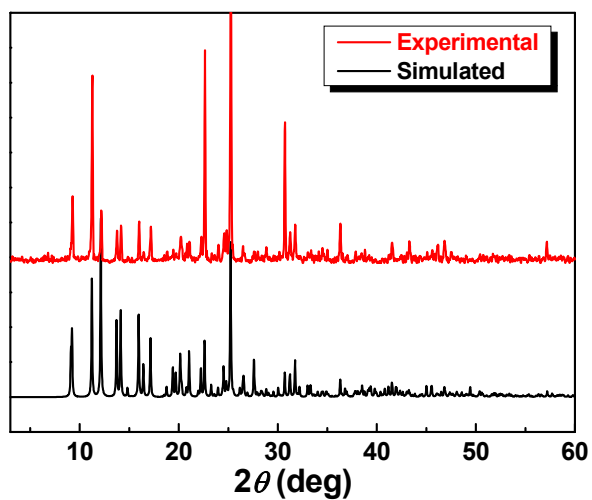
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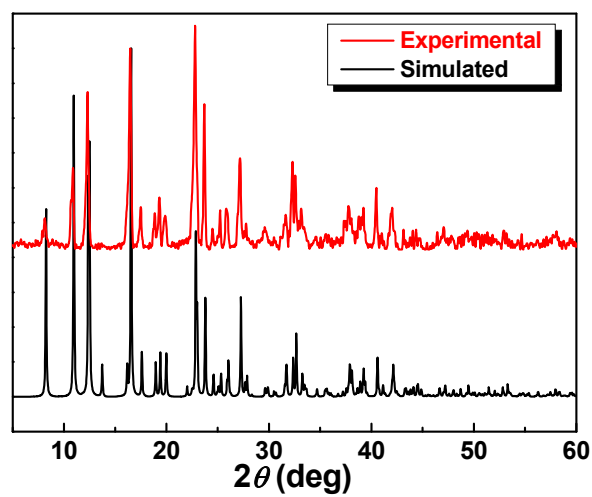
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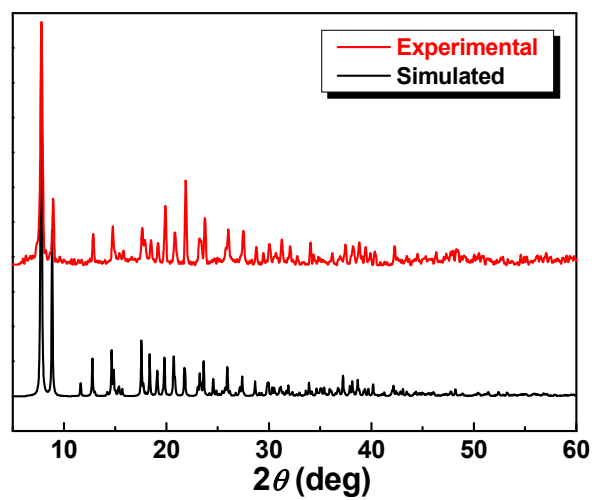
CrystEngComm



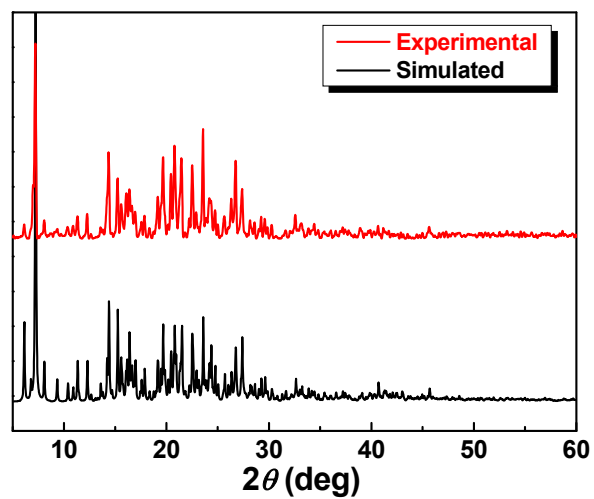
(a)



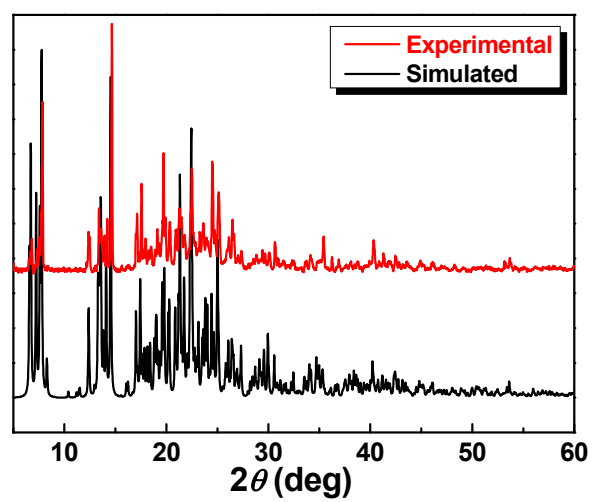
(b)



(c)



(d)



(e)

Fig. S1 PXRD patterns of (a) 1, (b) 2, (c) 3, (d) 4, and (e) 5.

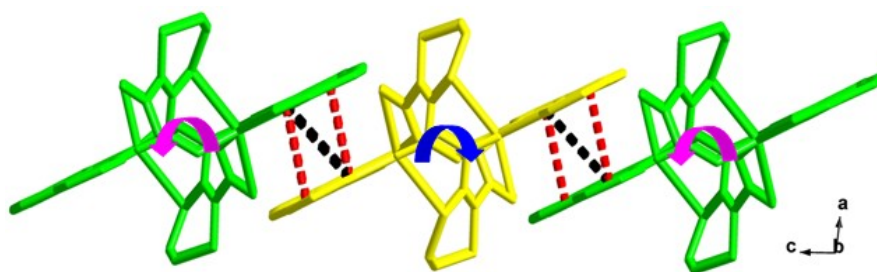


Fig. S2 The 2-D achiral network *via* aromatic interactions between the helical chains in **1**.

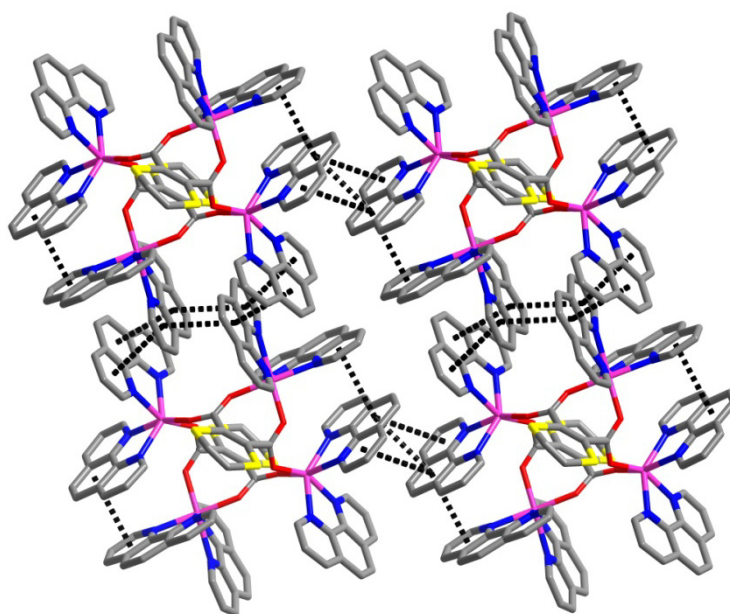


Fig. S3 The 2-D layer *via* multiple stacking interactions in **4**.

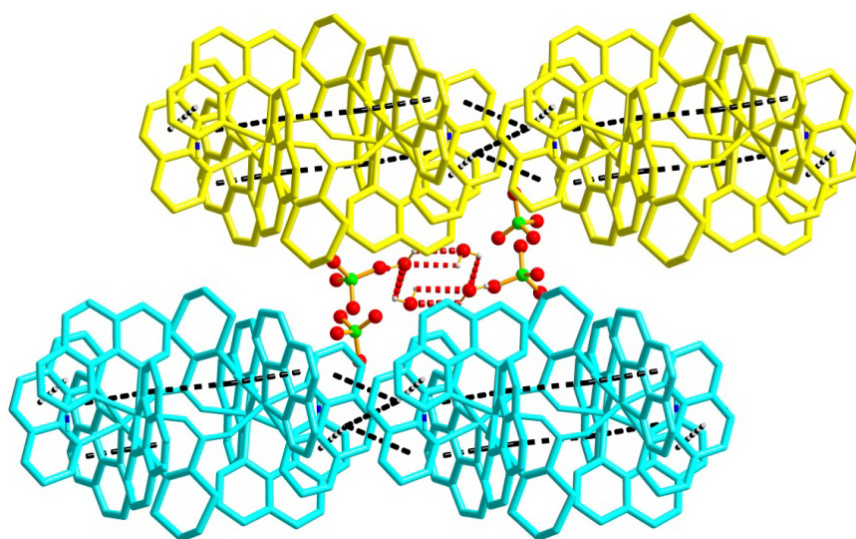


Fig. S4 Parallel stacking mode of the 2-D nets with hexameric units inset in **4**.

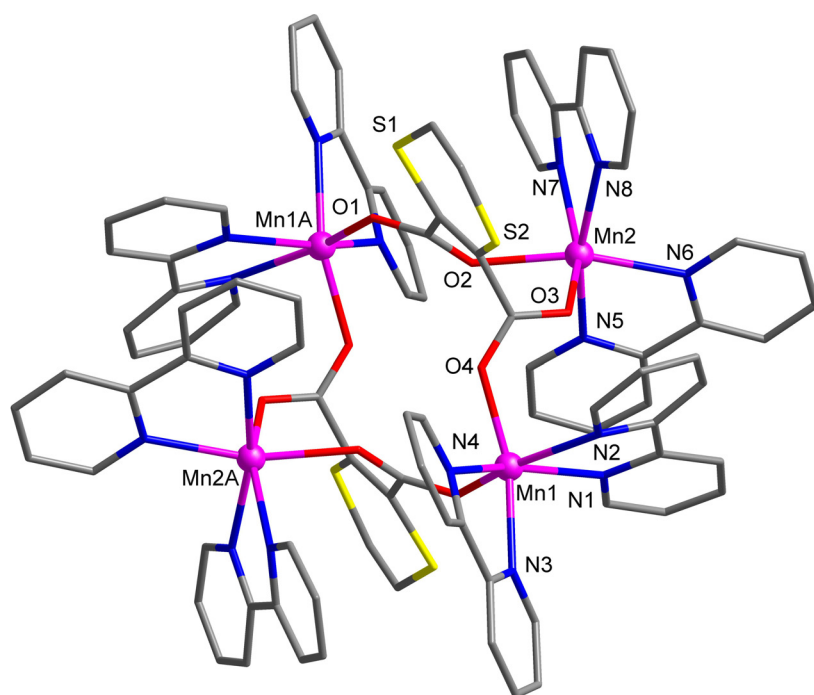
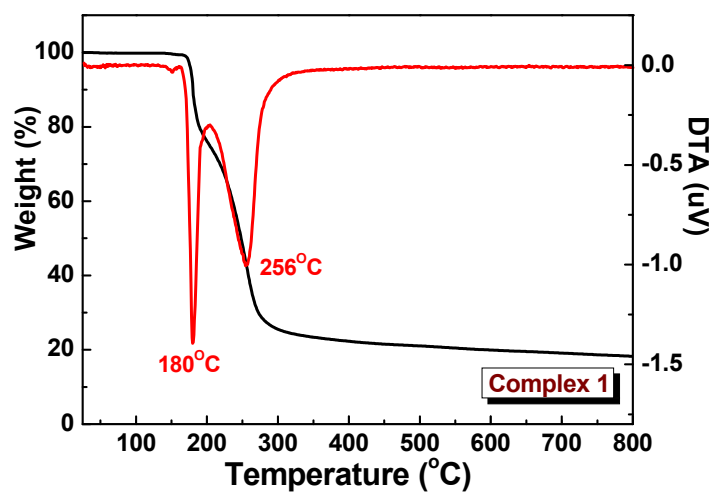
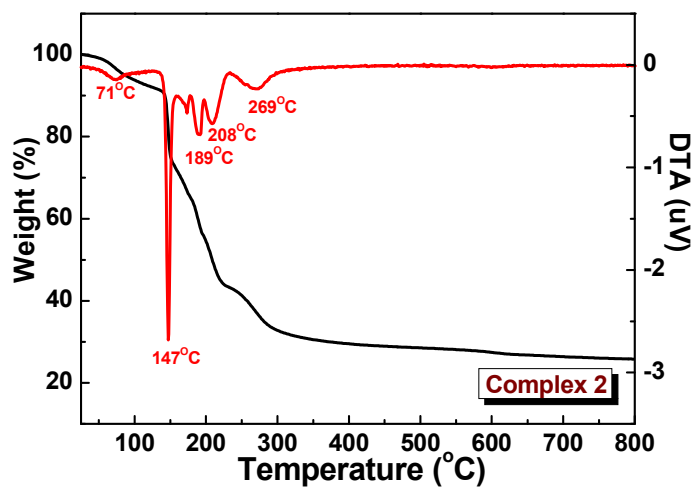


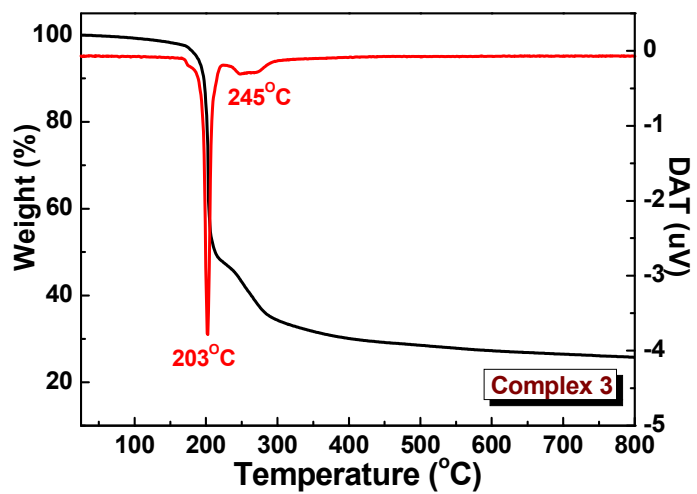
Fig. S5 The local coordination environments of Mn^{II} in **5** (symmetry code: A = $-x + 1, y + 1, -z$).



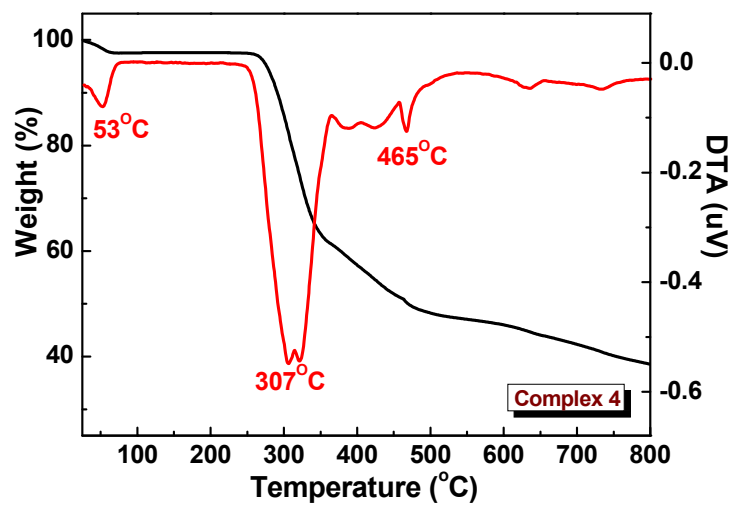
(a)



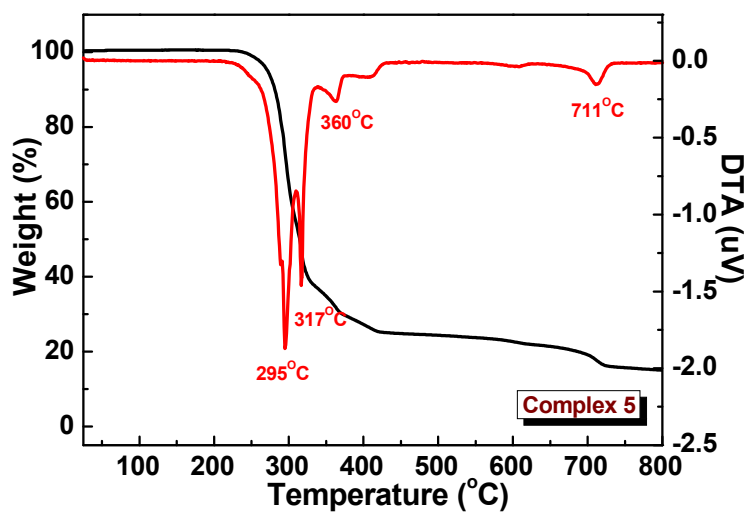
(b)



(c)



(d)



(e)

Fig. S6 TG-DTA curves of 1–5 (a–e).

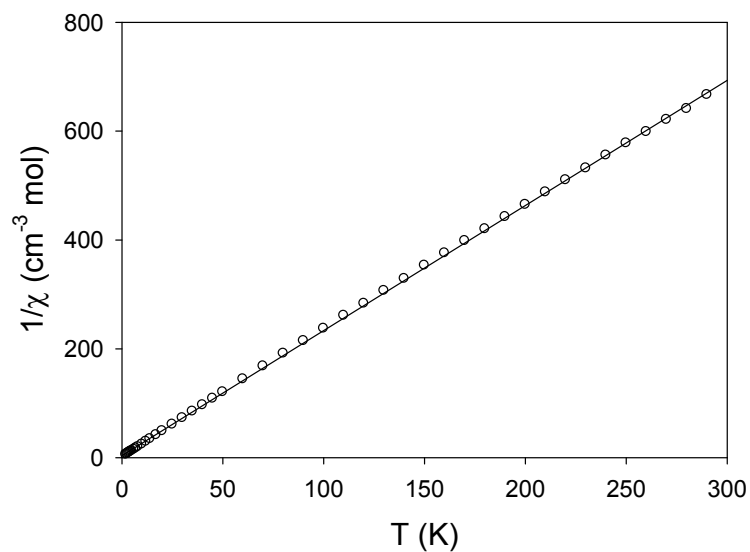


Fig. S7 Curie plot for **1**. The solid line is the best fitting to the Curie-Weiss law (see the text for fitting parameters).

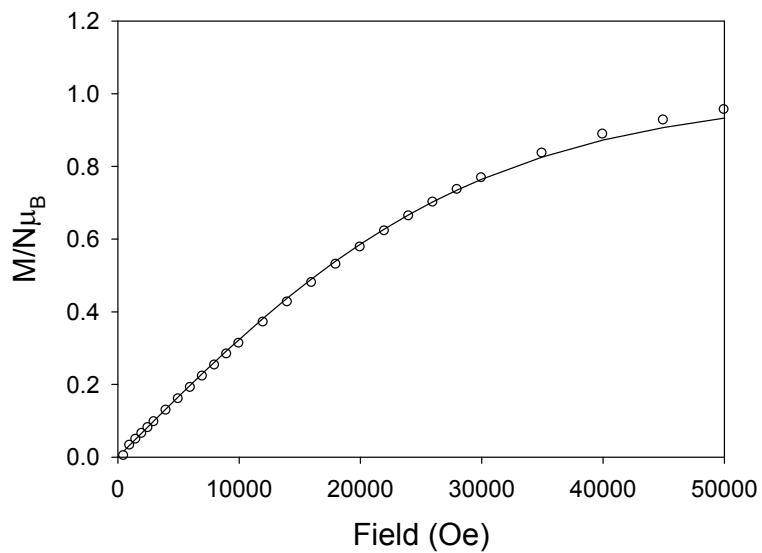


Fig. S8 Magnetization vs. field plot for **1** at 2 K. The solid line is the Brillouin function for $S = 1/2$ and $g = 2.0$.

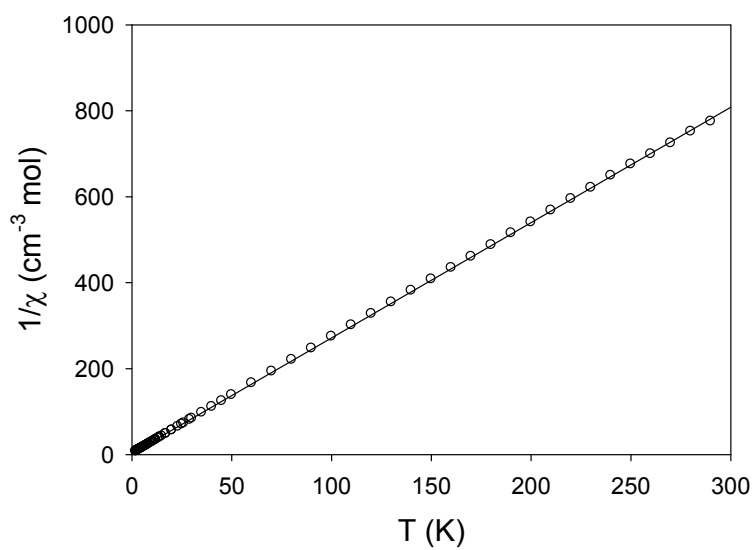


Fig. S9 Curie plot for **2**. The solid line is the best fitting to the Curie-Weiss law (see text for fitting parameters).

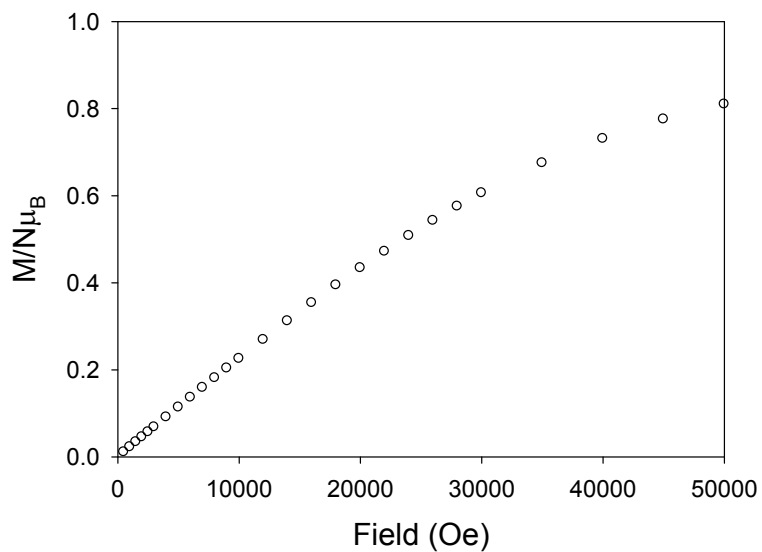


Fig. S10 Magnetization vs. field plot for **2** at 2 K.

Table S1 Selected bond distances (Å) and angles (°) for **1–5**.

1			
Cu1–O4 ^{#1}	1.9313(17)	Cu1–N1	2.007(2)
Cu1–O1	1.9547(17)	Cu1–N2	2.013(2)
Cu1–O2	2.6799(23)	Cu1–S1 ^{#1}	2.7690(8)
O4 ^{#1} –Cu1–O1	88.86(7)	N1–Cu1–N2	81.81(8)
O4 ^{#1} –Cu1–N1	175.26(8)	O4 ^{#1} –Cu1–S1 ^{#1}	80.20(6)
O1–Cu1–N1	94.88(8)	O1–Cu1–S1 ^{#1}	91.73(6)
O4 ^{#1} –Cu1–N2	94.16(8)	N1–Cu1–S1 ^{#1}	102.56(6)
O1–Cu1–N2	173.18(8)	N2–Cu1–S1 ^{#1}	94.80(6)
Symmetry code: #1 = -x + 2, y - 1/2, -z + 1/2.			
2			
Cu1–O1	1.928(6)	Cu1–N1	2.019(7)
Cu1–O4 ^{#1}	1.965(7)	Cu1–N2 ^{#2}	2.037(6)
Cu1–O5	2.8070(78)	Cu1–S1 ^{#1}	2.756(3)
O1–Cu1–O4 ^{#1}	171.3(3)	N1–Cu1–N2 ^{#2}	178.0(4)
O1–Cu1–N1	93.0(3)	O1–Cu1–S1 ^{#1}	95.7(2)
O4 ^{#1} –Cu1–N1	93.3(3)	O4 ^{#1} –Cu1–S1 ^{#1}	78.2(2)
O1–Cu1–N2 ^{#2}	86.7(3)	N1–Cu1–S1 ^{#1}	89.8(2)
O4 ^{#1} –Cu1–N2 ^{#2}	87.3(3)	N2 ^{#2} –Cu1–S1 ^{#1}	92.2(2)
Symmetry codes: #1 = x, y, z - 1; #2 = x - 1/2, y - 1/2, z.			
3			
Cu1–O1	1.902(2)	Cu2–O6 ^{#2}	1.918(2)
Cu1–O9	1.9132(19)	Cu2–O9	1.9359(18)
Cu1–O5	2.040(2)	Cu2–O9 ^{#2}	1.9481(17)
Cu1–O7 ^{#1}	2.0505(19)	Cu2–O4 ^{#1}	2.317(4)
Cu2–O8 ^{#1}	1.916(2)		
O1–Cu1–O9	172.39(9)	O6 ^{#2} –Cu2–O9	172.91(10)
O1–Cu1–O5	90.52(9)	O8 ^{#1} –Cu2–O9 ^{#2}	175.64(9)

O9–Cu1–O5	90.27(8)	O6 ^{#2} –Cu2–O9 ^{#2}	94.01(8)
O1–Cu1–O7 ^{#1}	93.05(8)	O9–Cu2–O9 ^{#2}	83.89(8)
O9–Cu1–O7 ^{#1}	91.02(8)	O8 ^{#1} –Cu2–O4 ^{#1}	94.79(12)
O5–Cu1–O7 ^{#1}	141.60(9)	O6 ^{#2} –Cu2–O4 ^{#1}	97.15(12)
O8 ^{#1} –Cu2–O6 ^{#2}	88.63(9)	O9–Cu2–O4 ^{#1}	89.58(11)
O8 ^{#1} –Cu2–O9	93.08(8)	O9 ^{#2} –Cu2–O4 ^{#1}	88.34(11)

Symmetry codes: #1 = $-x + 2, -y, -z$; #2 = $-x + 3, -y, -z$.

4

Mn1–O4 ^{#1}	2.114(3)	Mn2–O1	2.099(3)
Mn1–O2	2.133(3)	Mn2–O3	2.138(4)
Mn1–N1	2.253(4)	Mn2–N7	2.232(4)
Mn1–N4	2.283(4)	Mn2–N8	2.232(4)
Mn1–N2	2.318(4)	Mn2–N5	2.242(4)
Mn1–N3	2.329(4)	Mn2–N6	2.337(4)
O4 ^{#1} –Mn1–O2	92.52(12)	O1–Mn2–O3	85.94(14)
O4 ^{#1} –Mn1–N1	88.94(14)	O1–Mn2–N7	102.05(14)
O2–Mn1–N1	120.52(13)	O3–Mn2–N7	87.80(15)
O4 ^{#1} –Mn1–N4	114.41(14)	O1–Mn2–N8	95.68(14)
O2–Mn1–N4	84.48(14)	O3–Mn2–N8	162.22(14)
N1–Mn1–N4	145.97(15)	N7–Mn2–N8	74.53(16)
O4 ^{#1} –Mn1–N2	160.50(15)	O1–Mn2–N5	96.35(14)
O2–Mn1–N2	92.41(13)	O3–Mn2–N5	96.77(13)
N1–Mn1–N2	72.34(16)	N7–Mn2–N5	161.32(15)
N4–Mn1–N2	84.85(15)	N8–Mn2–N5	100.63(15)
O4 ^{#1} –Mn1–N3	87.03(13)	O1–Mn2–N6	168.65(14)
O2–Mn1–N3	153.22(14)	O3–Mn2–N6	96.10(13)
N1–Mn1–N3	86.25(14)	N7–Mn2–N6	89.19(14)
N4–Mn1–N3	71.48(15)	N8–Mn2–N6	85.79(13)
N2–Mn1–N3	96.89(13)	N5–Mn2–N6	72.34(14)

Symmetry code: #1 = $-x, -y + 2, -z$.

5

Mn1–O1	2.099(2)	Mn2–O3	2.135(2)
Mn1–O4 ^{#1}	2.099(2)	Mn2–O2	2.176(2)
Mn1–N1	2.252(3)	Mn2–N5	2.237(2)
Mn1–N3	2.268(3)	Mn2–N6	2.247(3)
Mn1–N4	2.283(3)	Mn2–N7	2.271(3)
Mn1–N2	2.386(2)	Mn2–N8	2.278(2)
O1–Mn1–O4 ^{#1}	96.43(8)	O3–Mn2–O2	83.98(8)
O1–Mn1–N1	88.49(9)	O3–Mn2–N5	97.08(9)
O4 ^{#1} –Mn1–N1	106.87(9)	O2–Mn2–N5	86.90(8)
O1–Mn1–N3	92.18(9)	O3–Mn2–N6	99.41(9)
O4 ^{#1} –Mn1–N3	157.05(10)	O2–Mn2–N6	159.53(8)
N1–Mn1–N3	94.56(10)	N5–Mn2–N6	72.66(9)
O1–Mn1–N4	115.39(9)	O3–Mn2–N7	153.37(9)
O4 ^{#1} –Mn1–N4	85.36(9)	O2–Mn2–N7	82.19(9)
N1–Mn1–N4	152.22(10)	N5–Mn2–N7	104.76(10)
N3–Mn1–N4	71.73(10)	N6–Mn2–N7	101.49(9)
O1–Mn1–N2	159.40(9)	O3–Mn2–N8	90.27(9)
O4 ^{#1} –Mn1–N2	87.00(8)	O2–Mn2–N8	105.31(8)
N1–Mn1–N2	71.12(9)	N5–Mn2–N8	166.39(9)
N3–Mn1–N2	92.39(9)	N6–Mn2–N8	94.89(9)
N4–Mn1–N2	85.09(9)	N7–Mn2–N8	71.72(10)

Symmetry code: #1 = $-x + 1, y - 1, -z$.

Table S2 Hydrogen-bonding geometry (Å, °) for complexes **2–4**.

D–H...A	<i>d</i>(D–H)	<i>d</i>(H...A)	<i>d</i>(H...A)	D–H...A
		2		
O5–H1W...O2	0.85	2.22	2.797	125
		3		
O10–H2W...O8	0.85	2.24	2.971	144
O9–H9...O2 ^{#1}	0.98	1.57	2.546	173
Symmetry code: #1 = $-x + 2, -y, -z$.				
		4		
O1W–H1W...O2W ^{#1}	0.85	2.36	2.728	107
O1W–H2W...O7	0.85	2.57	3.116	123
O2W–H3W...O1W ^{#1}	0.85	2.37	2.728	106
O2W–H4W...O1W ^{#2}	0.85	2.27	2.708	112
Symmetry codes: #1 = $-x + 1, -y + 1, -z + 1$; #2 = $x - 1, y, z$.				