Electronic Supplementary Information for A family of 3d metal clusters based on N–N single bonds bridged quasi-linear trinuclear cores: the Mn analogue displaying single-molecule magnet behavior

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Table of content:

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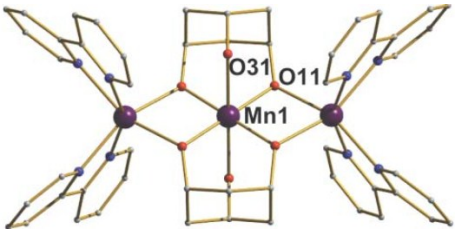
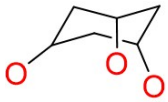
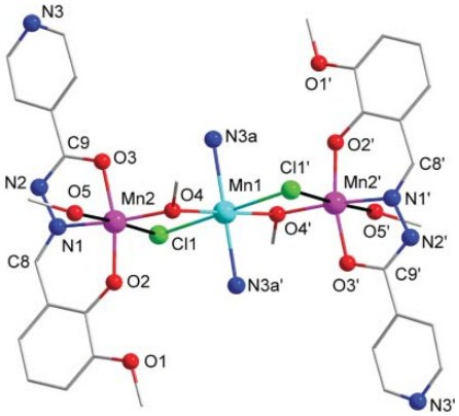
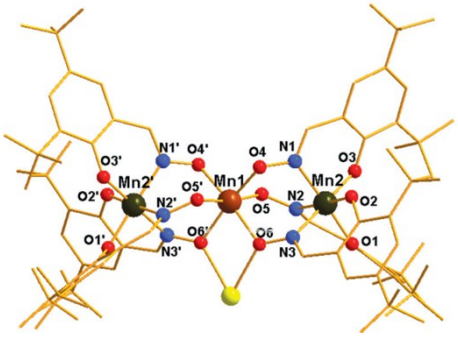
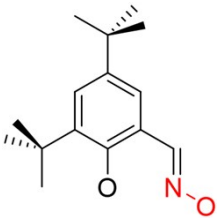
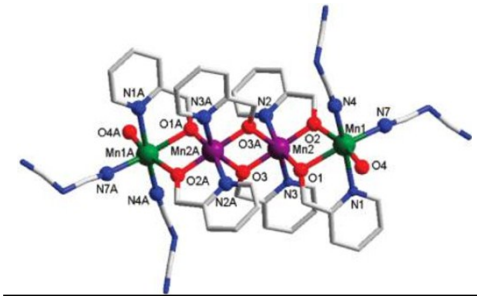
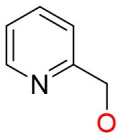
Table S1 Previous reported linear and quasi-linear Mn clusters showing SMM behavior

Molecular Structures	Formulas	Bridging Ligands[a]	Ref.
	$[Mn^{III}Mn_2^{II}(Hcht)_2(bpy)_4](ClO_4)_3 \cdot Et_2O \cdot 2MeCN$ (H_3cht = *cis,cis*-1,3,5-cyclohexanetriol)		7a
	$[Mn^{III}_2Mn^{II}(hmi)_2(OMe)_2Cl_2] \cdot MeOH$ (H_2hmi = ((2-hydroxy-3-methoxyphenyl)methylene)isonicotinohydrazine])	Cl^- and CH_3O^- ions	7b
	$[Mn_2^{IV}Mn^{III}Na(^tBuSao)_6(n\text{-}PrOH)_4 \cdot (n\text{-}PrOH)_4]$ ($^tBuSaoH_2$ = 3,5-di-tert-butyl-salicylaldoxime)		7c
	$[Mn^{III}_2Mn^{II}_2(hmp)_6(N(CN)_2)_4(H_2O)_2]$ (Hhmp = 2-(hydroxymethyl) pyridine; $N(CN)_2^-$ = dicyanamide anion)		7d

[a]The bridging atoms/groups were highlighted with red.

References

7. (a) A. Prescimone, J. Wolowska, G. Rajaraman, S. Parsons, W. Wernsdorfer, M. Murugesu, G. Christou, S. Piligkos, E. J. L. McInnes and E. K. Brechin, *Dalton Trans.,* 2007, 5282; (b) P. H. Lin, S. Gorelsky, D. Savard, T. J. Burchell, W. Wernsdorfer, R. Clérac and M. Murugesu, *Dalton Trans.,* 2010, **39**, 7650; (c) C. L. Zhou, Z. M. Wang, B. W. Wang and S. Gao, *Dalton Trans.,* 2012, **41**, 13620; (d) D. C. Li, H. S. Wang, S. N. Wang, Y. P. Pan, C. J. Li, J. M. Dou and Y. Song, *Inorg. Chem.,* 2010, **49**, 3688.

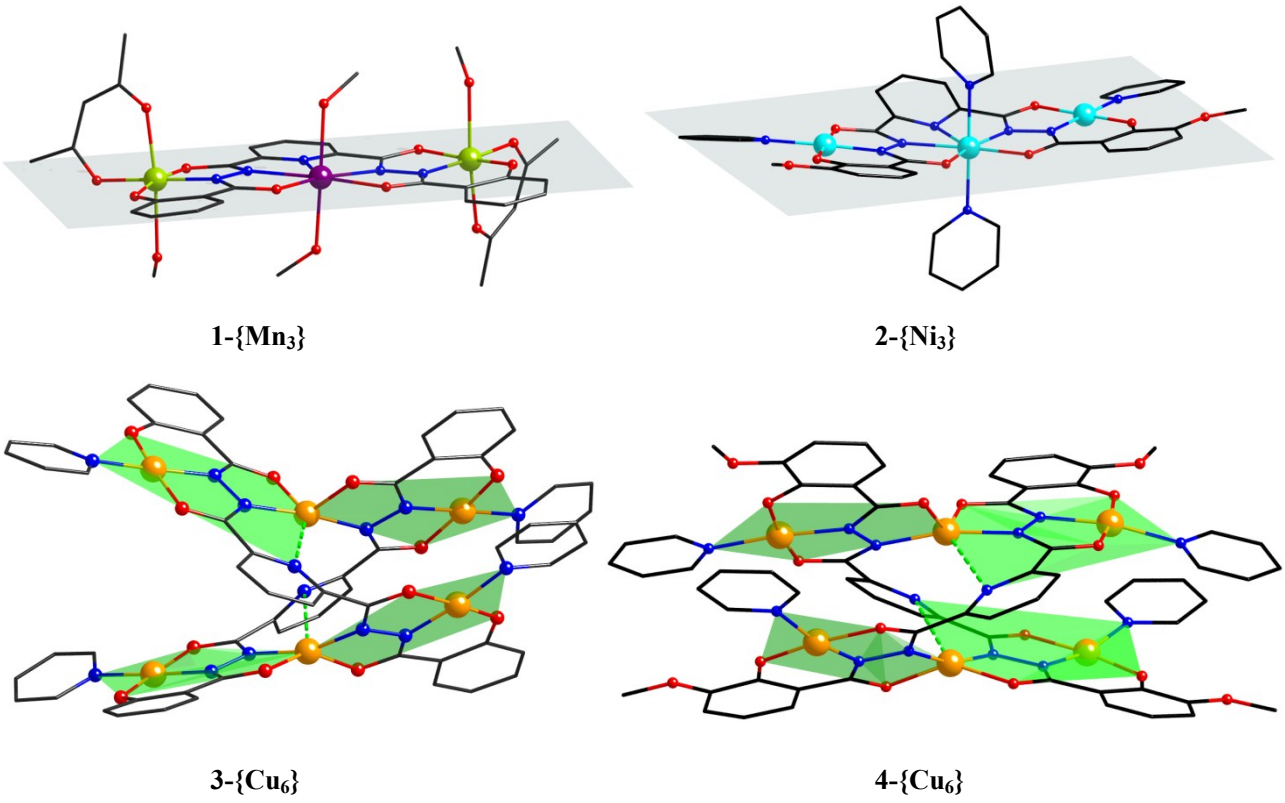


Fig. S1 The meaning plane composed of metal centers and their donors in equatorial positions for **1-4**.

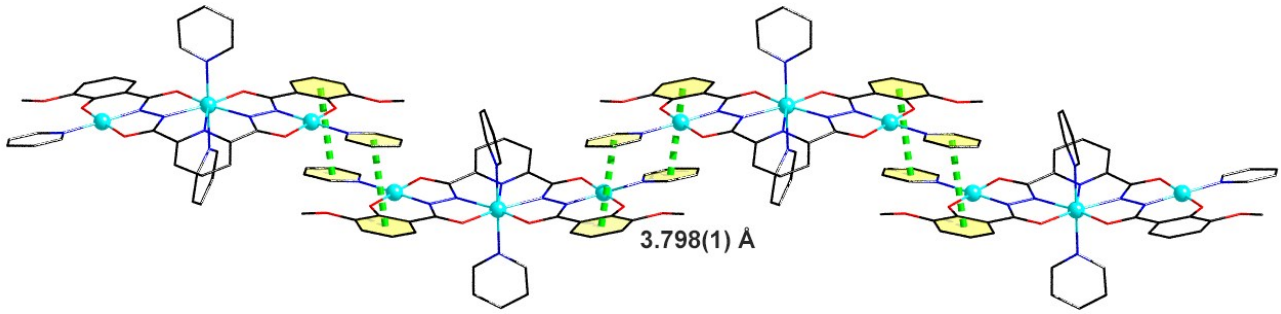


Fig. S2 Supramolecular chain along the *b*-axis linked together by π-π interactions in **2**.

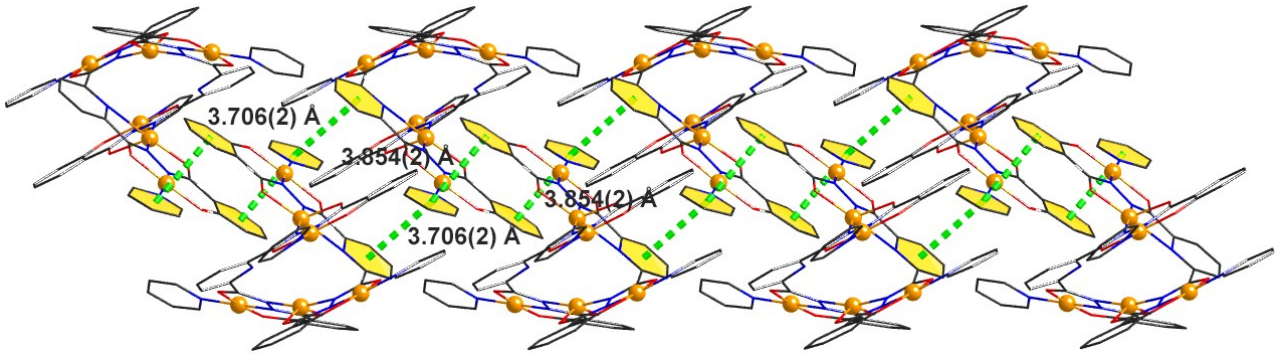


Fig. S3 Supramolecular chain linked by π-π interactions in **3** viewed along the *c*-axis.

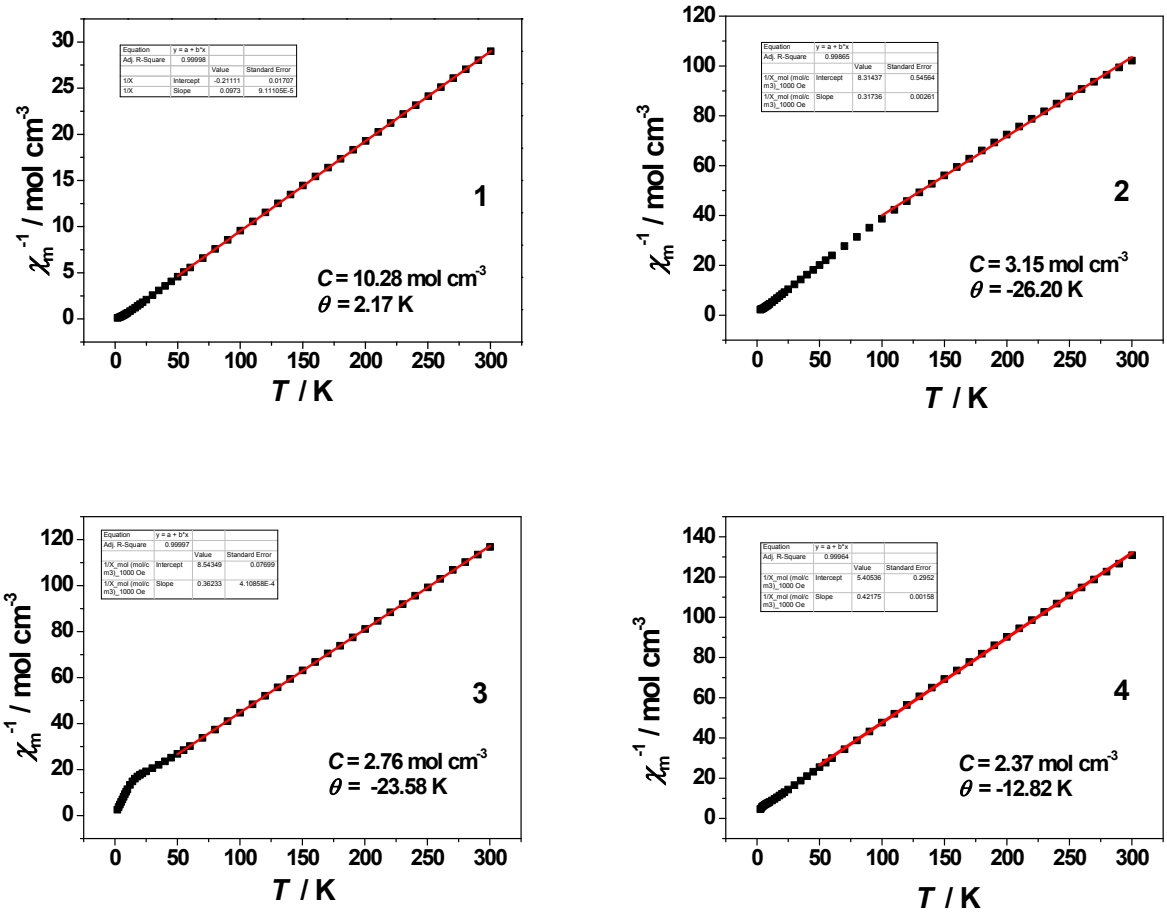


Fig. S4 Plots of χ_m^{-1}-T for **1-4**. The red lines represent the best fitting according to Curie-Weiss law.

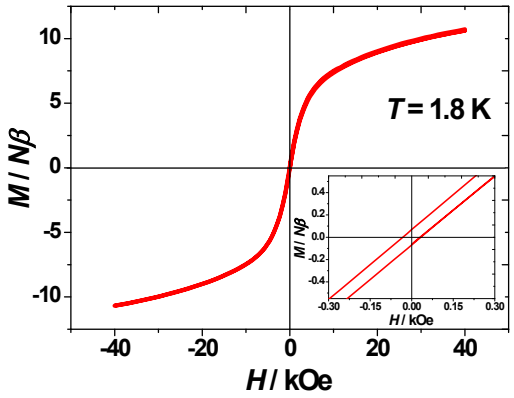


Fig. S5 Hysteresis loop of **1** recorded at 1.8 K and the expansion of hysteresis region (inset).

Table S2 The relative structural and magnetic parameters of **1–4**.

Main parameters	**1**	**2**	**3**	**4**
Structural				
M–N–N–M torsion angle (˚)	172.5	177.2	178.3, 167.6 170.8, 170.6	173.9, 175.2 172.7, 174.1
M···M distance (Å)	4.935	4.728	4.569, 4.564 4.545, 4.534	4.579, 4.585 4.585, 4.582
M-M-M angles (˚)	153.1	151.9	162.0, 171.4	175.4, 169.3
Angles between J-T axes (˚)	6.2	none	none	none
Magnetic				
S of 3d ions	2, 5/2	1	1/2	1/2
Expected $\chi_m T$ values at 300 K ($cm^3\ mol^{-1}\ K$)	10.375	3.0	2.5	2.5
Experimental $\chi_m T$ values at 300 K ($cm^3\ mol^{-1}\ K$)	10.35	2.94	2.57	2.29
C ($cm^3\ mol^{-1}$)	10.28	3.15	2.76	2.37
θ (K)	2.17	–26.20	–23.58	–12.82
J (cm^{-1})	5.1	–12.6	–5.2, –3.9, –4.7, –3.5	–11.1, –9.5, –10.9, –9.1
zJ (cm^{-1})	–0.12	–0.18	–0.27	–0.33
Expected *g* values	2	2.2	2	2
Fitted *g* values	1.99	2.2	2.1	2.1
Magnetic interactions	FM	AFM	AFM	AFM

Table S3 Data of π-π interactions for **2** and **3**.

Aromatic rings	Twist angle (˚)	Fold angle (˚)	Centroid-to-centroid distance (Å)
2			
C1-C6 and N3, C13-C17[a]	170.058	173.859	3.798
3			
N6, C23-C26 and C1-C6[b]	15.960	5.841	3.854
N6, C23-C26 and N3, C9-C13[c]	29.554	6.472	3.706

Symmetry code: (a) -*x*, 1-*y*, 1-*z*. (b) 1-*x*, -*y*, 1-*z*.; (c) 2-*x*, -*y*, 1-*z*.

Table S4 Crystal data and structure refinement parameters for **1-4**.

Identification	**1**	**2**	**3**	**4**
Empirical formula	$C_{35}H_{41}N_5O_{14}Mn_3$	$C_{43}H_{33}N_9O_8Ni_3$	$C_{62}H_{42}N_{14}O_{12}Cu_6$	$C_{71}H_{68}N_{16}O_{20}Cu_6$
Formula weight	920.55	981.93	1556.34	1846.67
Temp/K	296.15	150.15	150.15	150.15
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic
Space group	*Pbcn*	*Pnma*	$P\bar{1}$	$P2_1/c$
a/Å	17.0744(3)	17.9052(2)	11.9690(6)	14.6309(5)
b/Å	20.5494(4)	25.3476(2)	14.4468(6)	35.9987(10)
c/Å	11.4918(2)	8.99870(10)	17.6248(9)	14.3693(4)
α/°	90.00	90.00	89.892(4)	90.00
β/°	90.00	90.00	73.514(4)	90.793(2)
γ/°	90.00	90.00	82.879(4)	90.00
V/Å^3	4032.12(13)	4084.09(7)	2898.0(2)	7567.5(4)
Z	4	4	2	4
D_c/g cm^{-3}	1.516	1.597	1.784	1.536
*m*μ/mm^{-1}	0.996	1.436	2.242	1.731
F(000)	1892.0	2016.0	1564.0	3544.0
Reflections collected	41834	33538	26793	58702
Independent reflections	4993	3681	10172	13305
Data/restrains/parameters	4993/4/269	3681/6/314	10178/0/847	13305/0/968
R_{int}	0.0514	0.0311	0.0240	0.0720
GOF	1.104	1.067	1.065	1.028
Final *R* indexes ($I > 2\sigma(I)$)	$R_1 = 0.0414$, $wR_2 = 0.0924$	$R_1 = 0.0222$, $wR_2 = 0.0582$	$R_1 = 0.0312$, $wR_2 = 0.0757$	$R_1 = 0.0616$, $wR_2 = 0.1467$
Final *R* indexes (all data)	$R_1 = 0.0621$, $wR_2 = 0.1014$	$R_1 = 0.0237$, $wR_2 = 0.0590$	$R_1 = 0.0409$, $wR_2 = 0.0800$	$R_1 = 0.0975$, $wR_2 = 0.1594$

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Mn1-O1	1.8711 (17)	Mn1-O6	2.347 (2)	Mn2-O7	2.2105 (18)
Mn1-O3	1.9580 (16)	Mn1-N1	1.9305 (19)	Mn2-N2	2.2402 (18)
Mn1-O4	1.9251 (17)	Mn2-O2	2.2960 (16)	Mn2-N3	2.465 (3)
Mn1-O5	2.1612 (19)				
Bond Angle	Angle(˚)	Bond Angle	Angle(˚)	Bond Angle	Angle(˚)
O1-Mn1-O3	169.99 (7)	O4-Mn1-O6	85.83 (8)	O7^{a}-Mn2-O2	90.42 (7)
O1-Mn1-O4	93.66 (8)	O4-Mn1-N1	175.72 (8)	O7^{a}-Mn2-O7	175.07 (11)
O1-Mn1-O5	94.66 (8)	O5-Mn1-O6	173.68 (7)	O7^{a}-Mn2-N2	88.34 (7)
O1-Mn1-O6	84.95 (8)	N1-Mn1-O3	81.56 (7)	O7-Mn2-N2	89.56 (7)
O1-Mn1-N1	90.27 (8)	N1-Mn1-O5	93.49 (8)	O7-Mn2-N3	87.54 (6)
O3-Mn1-O5	91.61 (7)	N1-Mn1-O6	92.83 (8)	N2-Mn2-O2^{a}	162.08 (6)
O3-Mn1-O6	89.67 (7)	O2-Mn2-O2^{a}	93.69 (8)	N2-Mn2-O2	68.42 (6)
O4-Mn1-O3	94.36 (7)	O2-Mn2-N3	133.16 (4)	N2-Mn2-N2^{a}	129.48 (10)
O4-Mn1-O5	87.90 (7)	O7-Mn2-O2	92.95 (7)	N2-Mn2-N3	64.74 (5)

Table S5 Selected Bond Lengths (Å) and Bond Angles (°) of **1**.

Symmetry code: (a) −*x*, *y*, −*z*+3/2.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Ni1-O2	1.8208 (14)	Ni1-N3	1.9389 (18)	Ni2-N5	2.1227 (16)
Ni1-O4	1.8761 (15)	Ni2-O3	2.0695 (14)	Ni2-N6	2.0999 (16)
Ni1-N1	1.8271 (17)	Ni2-N2	2.1633 (17)		
Bond Angle	Angle(˚)	Bond Angle	Angle(˚)	Bond Angle	Angle(˚)
O2-Ni1-O4	177.27 (7)	N1-Ni1-N3	176.17 (8)	O3-Ni2-N6	89.60 (5)
O2-Ni1-N1	93.10 (7)	O3^{a}-Ni2-O3	89.90 (8)	N2-Ni2-N2^{a}	120.88 (9)
O2-Ni1-N3	89.85 (7)	O3-Ni2-N2	74.56 (6)	N5-Ni2-N2	91.03 (5)
O4-Ni1-N3	92.46 (7)	O3^{a}-Ni2-N2	164.32 (6)	N6-Ni2-N2	88.23 (5)
N1-Ni1-O4	84.65 (7)	O3-Ni2-N5	91.45 (5)	N6-Ni2-N5	178.51 (9)

Table S6 Selected Bond Lengths (Å) and Bond Angles (°) of **2**.

Symmetry code: (a) x, $-y+3/2$, z.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Cu1-O1	1.875 (2)	Cu3-O10	1.946 (2)	Cu5-O5	1.9941 (19)
Cu1-O3	1.975 (2)	Cu3-O12	1.872 (2)	Cu5-O8	1.982 (2)
Cu1-N1	1.892 (2)	Cu3-N12	1.902 (2)	Cu5-N4	1.907 (2)
Cu1-N6	1.981 (2)	Cu3-N14	2.010 (2)	Cu5-N9	1.913 (2)
Cu2-O2	2.033 (2)	Cu4-O7	1.888 (2)	Cu6-O4	1.996 (2)
Cu2-O11	2.043 (2)	Cu4-O9	1.987 (2)	Cu6-O6	1.889 (2)
Cu2-N2	1.927 (2)	Cu4-N8	1.889 (2)	Cu6-N5	1.888 (2)
Cu2-N11	1.928 (2)	Cu4-N13	1.981 (2)	Cu6-N7	1.978 (2)
Bond Angle	Angle(˚)	Bond Angle	Angle(˚)	Bond Angle	Angle(˚)
O1-Cu1-O3	174.18 (9)	O10-Cu3-N14	93.63 (10)	O8-Cu5-O5	148.13 (9)
O1-Cu1-N1	92.37 (10)	O12-Cu3-O10	174.62 (8)	N4-Cu5-O5	80.55 (9)
O1-Cu1-N6	91.82 (10)	O12-Cu3-N12	93.09 (10)	N4-Cu5-O8	102.29 (9)
O3-Cu1-N6	93.98 (9)	O12-Cu3-N14	91.75 (10)	N4-Cu5-N9	163.35 (11)
N1-Cu1-O3	81.89 (9)	N12-Cu3-O10	81.54 (9)	N9-Cu5-O5	105.76 (9)
N1-Cu1-N6	174.09 (11)	N12-Cu3-N14	174.38 (11)	N9-Cu5-O8	80.64 (9)
O2-Cu2-O11	123.04 (9)	O7-Cu4-O9	172.91 (8)	O6-Cu6-O4	173.15 (9)
N2-Cu2-O2	79.48 (9)	O7-Cu4-N8	91.46 (9)	O6-Cu6-N7	94.44 (10)
N2-Cu2-O11	105.06 (9)	O7-Cu4-N13	93.02 (10)	N5-Cu6-O4	81.86 (9)
N2-Cu2-N11	173.68 (11)	N8-Cu4-O9	81.79 (9)	N5-Cu6-O6	91.84 (9)
N11-Cu2-O2	100.74 (9)	N8-Cu4-N13	175.51 (10)	N5-Cu6-N7	173.16 (10)
N11-Cu2-O11	80.19 (9)	N13-Cu4-O9	93.72 (9)	N7-Cu6-O4	91.73 (9)

Table S7 Selected Bond Lengths (Å) and Bond Angles (°) of **3**.

Table S8 Selected Bond Lengths (Å) and Bond Angles (°) of **4**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Cu1-O2	1.874 (4)	Cu3-O13	1.965 (4)	Cu5-O6	1.960 (4)
Cu1-O4	1.966 (4)	Cu3-O15	1.890 (4)	Cu5-O11	1.982 (4)
Cu1-N1	1.892 (5)	Cu3-N12	1.897 (5)	Cu5-N4	1.951 (5)
Cu1-N6	1.982 (5)	Cu3-N14	1.984 (5)	Cu5-N9	1.952 (5)
Cu2-O3	2.012 (4)	Cu4-O10	1.880 (4)	Cu6-O5	1.964 (4)
Cu2-O14	2.003 (4)	Cu4-O12	1.976 (4)	Cu6-O7	1.897 (4)
Cu2-N2	1.941 (5)	Cu4-N8	1.896 (5)	Cu6-N5	1.881 (5)
Cu2-N11	1.945 (5)	Cu4-N13	1.993 (5)	Cu6-N7	1.993 (5)
Bond Angle	Angle(˚)	Bond Angle	Angle(˚)	Bond Angle	Angle(˚)
O2-Cu1-O4	171.53 (19)	O13-Cu3-N14	92.7 (2)	O6-Cu5-O11	144.93 (19)
O2-Cu1-N1	92.67 (19)	O15-Cu3-O13	172.09 (18)	N4-Cu5-O6	80.73 (19)
O2-Cu1-N6	93.0 (2)	O15-Cu3-N12	91.81 (18)	N4-Cu5-O11	105.98 (19)
O4-Cu1-N6	92.8 (2)	O15-Cu3-N14	94.2 (2)	N4-Cu5-N9	163.5 (2)
N1-Cu1-O4	81.85 (18)	N12-Cu3-O13	82.04 (17)	N9-Cu5-O6	103.07 (19)
N1-Cu1-N6	173.6 (2)	N12-Cu3-N14	169.5 (2)	N9-Cu5-O11	80.29 (19)
O14-Cu2-O3	135.29 (18)	O10-Cu4-O12	172.6 (2)	O5-Cu6-N7	92.56 (19)
N2-Cu2-O3	79.98 (18)	O10-Cu4-N8	91.4 (2)	O7-Cu6-O5	172.51 (19)
N2-Cu2-O14	102.74 (18)	O10-Cu4-N13	92.9 (2)	O7-Cu6-N7	94.3 (2)
N2-Cu2-N11	168.1 (2)	O12-Cu4-N13	94.2 (2)	N5-Cu6-O5	81.75 (18)
N11-Cu2-O3	106.75 (18)	N8-Cu4-O12	81.88 (19)	N5-Cu6-O7	92.16 (19)
N11-Cu2-O14	79.58 (17)	N8-Cu4-N13	170.6 (2)	N5-Cu6-N7	167.3 (2)