Electronic Supplementary Information (ESI)

A new strategy to obtain tetranuclear cobalt(II) metal-organic frameworks based on $[Co_4(\mu_3\text{-}OH)_2]$ cluster: synthesis, structures and properties

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Table S1. Selected bond lengths [Å] and angles [°] for **1- 3.**

1

Co(1)-O(6)#1	2.050(3)	Co(3)-O(14)	1.966(3)
Co(1)-O(13)#1	2.064(3)	Co(3)-O(8)	2.106(3)
Co(1)-O(13)	2.082(3)	Co(3)-N(4)#2	2.107(3)
Co(1)-O(2A)	2.092(5)	Co(3)-O(3)#1	2.142(3)
Co(1)-N(1)	2.105(3)	Co(3)-O(4)#1	2.175(3)
Co(1)-O(22)	2.160(7)	Co(3)-O(7)	2.258(3)
Co(1)-O(1)	2.267(3)	Co(4)-O(14)	1.967(3)
Co(2)-O(5)	2.005(3)	Co(4)-N(5)#2	2.097(3)
Co(2)-O(13)	2.072(2)	Co(4)-O(9)	2.101(3)
Co(2)-N(2)	2.098(3)	Co(4)-O(11)#3	2.120(3)
Co(2)-O(16)	2.127(3)	Co(4)-O(10)	2.251(3)
Co(2)-O(15)	2.132(3)	Co(4)-O(12)#3	2.251(3)
Co(2)-O(1)#1	2.150(3)		
O(6)#1-Co(1)-O(13)#1	96.06(11)	N(2)-Co(2)-O(1)#1	88.58(13)
O(6)#1-Co(1)-O(13)	172.49(11)	O(16)-Co(2)-O(1)#1	176.97(11)
O(13)#1-Co(1)-O(13)	80.31(11)	O(15)-Co(2)-O(1)#1	94.52(11)
O(6)#1-Co(1)-O(2A)	93.97(18)	O(14)-Co(3)-O(8)	103.95(12)
O(13)#1-Co(1)-O(2A)	139.64(18)	O(14)-Co(3)-N(4)#2	87.56(11)
O(13)-Co(1)-O(2A)	93.02(18)	O(8)-Co(3)-N(4)#2	108.53(11)
O(6)#1-Co(1)-N(1)	86.67(11)	O(14)-Co(3)-O(3)#1	113.78(12)
O(13)#1-Co(1)-N(1)	111.35(12)	O(8)-Co(3)-O(3)#1	133.14(11)
O(13)-Co(1)-N(1)	88.53(11)	N(4)#2-Co(3)-O(3)#1	100.07(12)
O(2A)-Co(1)-N(1)	108.18(19)	O(14)-Co(3)-O(4)#1	171.70(12)

O(6)#1-Co(1)-O(22)	89.4(2)	O(8)-Co(3)-O(4)#1	83.95(11)
O(13)#1-Co(1)-O(22)	164.2(2)	N(4)#2-Co(3)-O(4)#1	87.48(11)
O(13)-Co(1)-O(22)	95.8(2)	O(3)#1-Co(3)-O(4)#1	60.67(10)
O(2A)-Co(1)-O(22)	24.7(2)	O(14)-Co(3)-O(7)	96.13(10)
N(1)-Co(1)-O(22)	83.7(2)	O(8)-Co(3)-O(7)	60.00(10)
O(6)#1-Co(1)-O(1)	90.12(12)	N(4)#2-Co(3)-O(7)	168.48(11)
O(13)#1-Co(1)-O(1)	82.84(10)	O(3)#1-Co(3)-O(7)	88.45(11)
O(13)-Co(1)-O(1)	95.92(11)	O(4)#1-Co(3)-O(7)	90.02(11)
O(2A)-Co(1)-O(1)	58.11(18)	O(14)-Co(4)-N(5)#2	88.53(11)
N(1)-Co(1)-O(1)	165.69(12)	O(14)-Co(4)-O(9)	107.01(11)
O(22)-Co(1)-O(1)	82.3(2)	N(5)#2-Co(4)-O(9)	96.87(11)
O(5)-Co(2)-O(13)	93.83(11)	O(14)-Co(4)-O(11)#3	112.06(11)
O(5)-Co(2)-N(2)	177.00(12)	N(5)#2-Co(4)-O(11)#3	113.59(11)
O(13)-Co(2)-N(2)	89.00(10)	O(9)-Co(4)-O(11)#3	130.12(10)
O(5)-Co(2)-O(16)	88.54(13)	O(14)-Co(4)-O(10)	165.70(11)
O(13)-Co(2)-O(16)	91.55(11)	N(5)#2-Co(4)-O(10)	87.61(10)
N(2)-Co(2)-O(16)	92.36(12)	O(9)-Co(4)-O(10)	59.87(9)
O(5)-Co(2)-O(15)	90.06(11)	O(11)#3-Co(4)-O(10)	82.07(10)
O(13)-Co(2)-O(15)	176.11(10)	O(14)-Co(4)-O(12)#3	94.08(10)
N(2)-Co(2)-O(15)	87.11(11)	N(5)#2-Co(4)-O(12)#3	173.44(11)
O(16)-Co(2)-O(15)	88.40(11)	O(9)-Co(4)-O(12)#3	88.13(10)
O(5)-Co(2)-O(1)#1	90.66(14)	O(11)#3-Co(4)-O(12)#3	59.85(9)
O(13)-Co(2)-O(1)#1	85.59(10)	O(10)-Co(4)-O(12)#3	91.26(10)
		2	
Co(1)-O(1)#1	2.030(2)	Co(3)-O(3)	2.241(2)
Co(1)-O(5)#2	2.163(3)	Co(3)-O(4)	2.166(2)
Co(1)-O(6)#2	2.295(3)	Co(3)-O(8)#6	2.046(3)
Co(1)-O(7)	2.025(2)	Co(3)-O(10)	2.010(2)
Co(1)-O(21)	2.094(2)	Co(3)-O(13)	2.111(2)
Co(1)-N(1)#3	2.125(2)	Co(3)-N(5)	2.127(3)
Co(2)-O(2)#1	2.158(2)	Co(4)-O(9)	2.123(4)
Co(2)-O(7)#4	2.123(2)	Co(4)-O(10)	2.039(2)
Co(2)-O(7)	2.085(2)	Co(4)-O(10)#6	2.119(2)
Co(2)-O(11)	2.055(2)	Co(4)-O(14)#6	2.042(3)
Co(2)-O(19)	2.110(2)	Co(4)-O(20)	2.136(3)
Co(2)-N(2)#5	2.148(2)	Co(4)-N(6)	2.147(3)
O(1)#1-Co(1)-O(5)	154.81(7)	O(4)-Co(3)-O(3)	59.70(7)
O(1)#1-Co(1)-O(6)#6	96.14(7)	O(10)-Co(3)-O(13)	88.61(10)
O(1)#1-Co(1)-O(21)	88.41(8)	O(8)#6-Co(3)-O(3)	150.63(7)
O(1)#1-Co(1)-N(1)#3	87.63(8)	O(8)#6-Co(3)-O(4)	90.94(7)
O(5)#2-Co(1)-O(6)#2	58.72(7)	O(8)#6-Co(3)-O(13)	89.09(7)
O(7)-Co(1)-O(1)#1	105.47(7)	O(8)#6-Co(3)-N(5)	89.45(8)
O(7)-Co(1)-O(5)#2	99.66(7)	O(10)-Co(3)-O(3)	89.90(7)
O(7)-Co(1)-O(6)#2	158.38(7)	O(10)-Co(3)-O(4)	149.17(7)

O(7)-Co(1)-O(21)	93.47(7)	O(10)-Co(3)-O(8)#6	119.36(7)
O(7)-Co(1)-N(1)#3	88.49(7)	O(10)-Co(3)-O(13)	88.60(7)
O(21)-Co(1)-O(5)#2	88.52(8)	O(10)-Co(3)-N(5)	88.51(7)
O(21)-Co(1)-O(6)#2	86.72(7)	O(13)-Co(3)-O(3)	89.25(7)
O(21)-Co(1)-N(1)#3	175.93(9)	O(13)-Co(3)-O(4)	86.01(7)
N(1)#3-Co(1)-O(5)#2	94.67(8)	O(13)-Co(3)-N(5)	175.60(7)
N(1)#3-Co(1)-O(6)#2	92.77(7)	N(5)-Co(3)-O(3)	94.05(8)
O(7)-Co(2)-O(2)#1	90.42(6)	N(5)-Co(3)-O(4)	98.16(8)
O(7)#4-Co(2)-O(2)#1	96.25(6)	O(9)-Co(4)-O(20)	83.19(7)
O(7)-Co(2)-O(7)#4	83.31(7)	O(9)-Co(4)-N(6)	167.64(7)
O(7)-Co(2)-O(19)	169.54(8)	O(10)#6-Co(4)-O(9)	96.95(7)
O(7)#4-Co(2)-N(5)#5	86.02(7)	O(10)-Co(4)-O(9)	90.35(7)
O(7)-Co(2)-N(2)#5	92.94(7)	O(10)-Co(4)-O(10)#6	80.32(7)
O(11)-Co(2)-O(2)#1	85.99(7)	O(10)-Co(4)-O(14)#6	169.89(7)
O(11)-Co(2)-O(7)#4	172.09(7)	O(10)#6-Co(4)-O(20)	177.04(8)
O(11)-Co(2)-O(7)	104.29(7)	O(10)-Co(4)-O(20)	96.73(8)
O(11)-Co(2)-O(19)	85.95(8)	O(10)#6-Co(4)-N(6)	94.65(7)
O(11)-Co(2)-N(2)#5	91.35(8)	O(10)-Co(4)-N(6)	87.42(7)
O(19)-Co(2)-O(2)#1	85.11(7)	O(14)#6-Co(4)-O(9)	93.20(7)
O(19)-Co(2)-O(7)#4	86.69(7)	O(14)#6-Co(4)-O(10)#6	89.86(7)
O(19)-Co(2)-N(2)#5	91.92(8)	O(14)#6-Co(4)-O(20)	93.08(8)
N(2)#5-Co(2)-O(2)#1	176.14(7)	O(14)#6-Co(4)-N(6)	91.06(8)
		O(20)-Co(4)-N(6)	85.00(8)
		3	
Co(1)-O(7)#1	2.056(3)	Co(2)-O(7)	1.991(3)
Co(1)-O(1)	2.069(3)	Co(2)-O(6)#2	2.045(3)
Co(1)-O(7)	2.097(3)	Co(2)-O(2)	2.112(3)
Co(1)-N(1)	2.123(4)	Co(2)-O(3)#3	2.122(3)
Co(1)-O(5)#2	2.130(3)	Co(2)-N(2)#1	2.154(4)
Co(1)-O(8)	2.139(4)	Co(2)-O(4)#3	2.319(3)
O(7)#1-Co(1)-O(1)	173.20(12)	O(7)-Co(2)-O(6)#2	119.55(12)
O(7)#1-Co(1)-O(7)	80.44(12)	O(7)-Co(2)-O(2)	88.88(13)
O(1)-Co(1)-O(7)	93.08(12)	O(6)#2-Co(2)-O(2)	85.44(13)
O(7)#1-Co(1)-N(1)	87.15(13)	O(7)-Co(2)-O(3)#3	143.83(12)
O(1)-Co(1)-N(1)	91.02(14)	O(6)#2-Co(2)-O(3)#3	96.61(13)
O(7)-Co(1)-N(1)	91.88(13)	O(2)-Co(2)-O(3)#3	94.65(13)
O(7)#1-Co(1)-O(5)#2	92.21(12)	O(7)-Co(2)-N(2)#1	87.89(13)
O(1)-Co(1)-O(5)#2	90.52(13)	O(6)#2-Co(2)-N(2)#1	85.60(14)
O(7)-Co(1)-O(5)#2	96.07(12)	O(2)-Co(2)-N(2)#1	167.43(13)
N(1)-Co(1)-O(5)#2	171.81(13)	O(3)#3-Co(2)-N(2)#1	95.13(14)
O(7)#1-Co(1)-O(8)	91.36(13)	O(7)-Co(2)-O(4)#3	85.39(12)
O(1)-Co(1)-O(8)	95.02(14)	O(6)#2-Co(2)-O(4)#3	154.85(13)
O(7)-Co(1)-O(8)	171.47(13)	O(2)-Co(2)-O(4)#3	92.42(13)
N(1)-Co(1)-O(8)	85.34(15)	O(3)#3-Co(2)-O(4)#3	58.53(12)

O(5)#2-Co(1)-O(8)	86.51(14)	N(2)#1-Co(2)-O(4)#3	99.42(14)

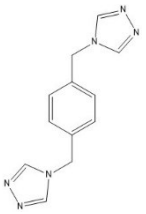
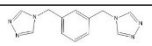
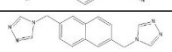
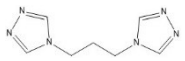
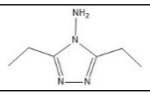
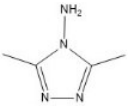
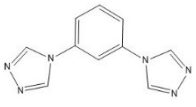
Symmetry transformations used to generate equivalent atoms: #1 -x, -y+1, -z; #2 -x+1, -y+1, -z+1; #3 -x, -y-1,-z+1 for **1**; #1 -x+1, -y+2, -z+2; #2 x, y, z+1; #3 x-1, y+1, z+1; #4 -x+1, -y+2, -z+3; #5 -x+2, -y+1, -z+2; #6 -x+1, -y+1, -z+2; #7 x, y, z-1; #8 x+1, y-1, z-1 for **2**; #1 -x, -y+1, -z+1; #2 x-1/2, -y+1/2, z-1/2; #3 x+1/2, -y+1/2, z-1/2; #4 x-1/2, -y+1/2, z+1/2; #5 x+1/2, -y+1/2, z+1/2; #6 -x+1, -y+1, -z+2 for **3**.

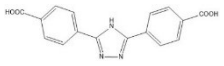
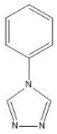
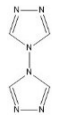
Table S2. Hydrogen bonds for **1**- **3** (Å and °).

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
	1			
O(13)-H(1W)…O(21)	0.895(19)	2.10(2)	2.963(9)	160(4)
O(14)-H(2W)…O(16)#4	1.049(16)	2.463(17)	3.511(4)	177(3)
O(15)-H(3W)…O(18)	0.884(18)	1.87(2)	2.721(4)	161(4)
O(15)-H(4W)…O(12)#5	0.881(18)	1.91(2)	2.770(4)	164(4)
O(16)-H(5W)…O(19)#6	0.880(19)	1.84(2)	2.703(5)	168(4)
O(16)-H(6W)…O(12)#5	0.891(19)	1.93(2)	2.768(4)	157(4)
O(17)-H(7W)…O(7)#6	0.91(2)	2.30(2)	2.926(5)	125(2)
O(17)-H(8W)…O(22)	0.92(2)	1.82(5)	2.611(9)	143(6)
O(18)-H(9W)…O(10)#5	0.893(19)	1.96(2)	2.846(4)	173(5)
O(18)-H(10W)…O(4)#1	0.889(19)	1.94(3)	2.788(4)	160(5)
O(19)-H(11W)…O(22)#4	0.92(2)	1.54(3)	2.441(10)	165(6)
O(19)-H(12W)…O(7)	0.90(2)	1.85(3)	2.735(5)	167(6)
	2			
O(19)-H(19A)…O(5)#1	0.91	1.91	2.717(3)	147(2)
O(20)-H(20B)…O(17)#2	0.93	2.11	2.921(8)	145(8)
O(20)-H(20B)…O(17A)#2	0.93	2.57	3.32(2)	137(6)
O(21)-H(21B)…O(12)	0.89	1.77	2.628(3)	161(4)
	3			
O(7)-H(7)…O(5)#1	0.887(17)	2.71(2)	3.015(3)	102(2)
O(8)-H(8B)…O(4)#2	0.858(17)	2.25(4)	2.992(3)	144(3)

Symmetry transformations used to generate equivalent atoms: #1 -x, -y+1, -z; #2 -x+1, -y+1, -z+1; #3 -x, -y-1, -z+1; #4 x, y-1, z; #5 -x, -y, -z+1; #6 x, y+1, z for **1**; #1 -x, -y+2, -z+2; #2 x+1, y, z; #3 x, y-1, z; #4 -x+1, -y+1, -z+1; #5 -x+2, -y+1, -z+2; for **2**; #1 -x+1/2, y+1/2, -z+3/2; #2 -x-1/2, y+1/2, -z+3/2 for **3**.

Table 3. The bond angles and the atom distances selected from different coordination quadrangle form by trizole ligands.

Compound	∠M-N-N (°)	d(M-N) (Å)	d(M-M) (Å)	d(N-N) (Å)	1,2,4-Triazole ligand	Ref.
1	121.889,121.540	2.098,2.106	3.570	1.377		This work
	118.889,120.033	2.107,2.097	3.468	1.384		
2	118.641,120.235	2.145,2.126	3.532	1.384		
	120.444,119.475	2.122,2.147	3.511	1.372		
3	119.870,119.372	2.154,2.123	3.530	1.389		
$\{[Cu(L)(ClO_4)]\bullet DMF\bullet H_2O\}_n$	126.332,127.088	2.028,2.043	3.780	1.377		9a
$\{[Cu_2(L)_2(ClO_4)_2]\bullet 4DMF\bullet H_2O\}_n$	123.795,124.730	2.031,2.025	3.663	1.373		
$\{[Cu(L)(ClO_4)]\bullet DMA\bullet H_2O\}_n$	124.253,124.113	2.023,2.021	3.663	1.386		
$\{[Cu(L)(ClO_4)]\bullet NMP\bullet H_2O\}_n$	128.607,127.390	2.068,2.058	3.959	1.379		
$\{[Cu(L)(ClO_4)]\bullet 3NMP\}_n$	126.833,123.174	2.037,2.023	3.736	1.399		
	125.098,125.036	2.057,2.031		1.387		
$\{[Cu_2(2a)(Br)_2]\bullet DMF\}_n$	122.620	1.970	3.515	1.390		9b
$\{[Ag_2(2a)(NO_3)_2]\bullet NMP\}_n$	123.620,121,916	2.195,2.206	3.753	1.368		
$\{[Cu_2(2a)(SO_4)(OH)_2(H_2O)_2]\bullet H_2O\}_n$	119.836,119.604	1.996,1.984	3.362	1.388		
	121.158,120.185	1.986,1.990	3.417			
$\{[Cu_2(2b)(Br)_2]\bullet DMF\}_n$	123.120	1.985	3.546	1.377		9b
$\{[Ag_2(2c)(NO_3)_2]\bullet NMP\}_n$	125.175,125.975	2.149,2.144	3.945	1.420		
$\{[Cu_4(OH)_2(H_2O)_2][Cu_4(OH)_2\}(tr_2pr)_2(Hadtc)_4]\bullet 2H_2O\}_n$	120.085,120.795	1.988,2.009	3.392	1.367		7a
	119.941,123.433	1.997,1.983	3.459	1.369		
$\{[Cu_4(OH)_2(tr_2ad)_2(Hadtc)_2(H_2O)_2]\bullet 3H_2O\}_n$	109.828,120.766	2.334,1.987	3.342	1.382		
	112.858,120.563	2.271,1.981	3.331	1.379		
$[Cu_3(\mu_2\text{-}OH)(\mu\text{-}adetrz)_2(piv)_5(H_2O)]\bullet 6.5H_2O$	115.530,118.174	2.260,1.988	3.339	1.389		7b
	115.587,116.895	2.017,2.028	3.189	1.398		
$[Cu_4(\mu_3\text{-}OH)_2(\mu\text{-}atrz)_2(\mu\text{-}piv)_4(piv)_2]\bullet 2MeOH\bullet H_2O$	124.901,119.161	1.956,2.013	3.393	1.289		
$[Cu_4(\mu_3\text{-}OH)_2(\mu\text{-}tbtrz)2(\mu\text{-}piv)_2(piv)_4]\bullet 4H_2O$	120.592,119.648	1.981,1.982	3.389	1.375		
$[Cu_4(\mu_3\text{-}O)_2(\mu\text{-}admtrz)_4(admtrz)_2(\mu\text{-}piv)_2(piv)_2]\bullet 2[Cu_2(\mu\text{-}H_2O)(\mu\text{-}admtrz)(piv)_4]\bullet 13H_2O$	116.554,118.947	2.044,1.992	3.274	1.354		
	114.177,111.682	2.008,2.450	3.278	1.410		
$\{[Cd(\mu_2\text{-}L)(\mu_4\text{-}L)](BF_4)_2\}_n$	129.007,123.684	2.303,2.329	4.136	1.388		15a
	125.604,125.006	2.382,2.335		1.408		
	126.126,124.870	2.333,2.385		1.388		
$\{[Cd(\mu_2\text{-}L)(\mu_4\text{-}L)](ClO_4)_2\}_n$	128.371,124.661	2.316,2.305	4.155	1.391		
	127.250,123.666	2.386,2.347		1.399		

	125.173,126.317	2.386,2.356		1.381		
$\{[Cd_3(\mu_3\text{-}L)_6](NO_3)_6\}_n$	123.172,128.986	2.335,2.350	4.140	1.391		
$\{[Zn_4L_2(\mu_2\text{-}O)_2(H_2O)_5]\bullet 3H_2O\}_n$	116.283,114.983	2.060,2.069	3.184	1.391		15b
	116.224,112.345	2.034,2.024	3.136	1.422		
$\{[Co(atz)(L1)_{0.5}]\bullet DMF\}_n$	124.025,130.879	2.005,2.032	3.861	1.405		15c
$\{[Co(atz)(L2)_{0.5}]\bullet DMF\}_n$	132.043,122.586	2.045,1.996	3.867	1.396		
$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\bullet CH_3OH \bullet CH_3CH_2OH$ 100K	122.987,129.208	2.235,2.031	3.919	1.406		15d
	122.271,130.055	2.198,2.021		1.428		
	124.676,127.825	2.210,2.040		1.401		
$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\bullet CH_3OH \bullet CH_3CH_2OH$ 296K	126.041,127.084	2.208,2.213	3.998	1.364		
	127.427,125.718	2.198,2.217		1.366		
	128.877,123.772	2.195,2.225		1.380		
$[Fe_2(\mu_2\text{-}L)_3(L)_2(NCS)_4]\bullet 2CH_3CH_2OH$	124.506,125.934	2.065,2.101	3.804	1.389		
	125.776,125.067	2.084,2.098		1.376		
	127.373,122.890	2.059,2.128		1.385		
$[Ni_3(\mu_2\text{-}L)_6(L)_4(H_2O)_2](NO_3)_6\bullet 15.5H_2O$	124.782,125.391	2.093,2.050	3.772	1.390		
	124.092,125.950	2.076,2.066		1.391		
	124.109,125.165	2.111,2.060		1.399		
$\{[Cu_3(\mu_3\text{-}OH)][Cu_3(\mu_3\text{-}O)][(\mu_4\text{-}btr)_3(H_2O)_4(OH)_2Cl_6]Cl\bullet 0.5H_2O\}_n$	118.772,121.506	2.003,1.996	3.406	1.386		15e
$\{[Cu_3(\mu_3\text{-}OH)]_2[(\mu_3\text{-}btr)_6(\mu_4\text{-}btr)(\mu\text{-}Br)Br_4]Br_5\bullet 6H_2O\}_n$	120.835,120.835	2.000,2.000	3.447	1.396		
	120.181,120.696	2.012,2.212	3.414	1.373		
$\{[Cu_3(\mu_3\text{-}OH)]_2[(\mu_3\text{-}btr)_6(\mu_4\text{-}btr)(\mu\text{-}Cl)Cl_4]Cl_5\bullet 8H_2O\}_n$	120.431,119.758	2.047,2.015	3.437	1.397		
	116.837,118.234	2.338,2.108		1.376		
	120.370,119.225	2.015,2.044	3.447	1.400		
	120.793,121.924	1.998,2.135	3.586	1.393		
	121.525,113.483	2.055,2.416	3.455	1.386		
	118.590,121.354	2.013,2.107		1.395		
	121.675,122.809	2.037,2.055	3.571	1.387		
	119.095,121.110	2.038,2.038	3.432	1.378		

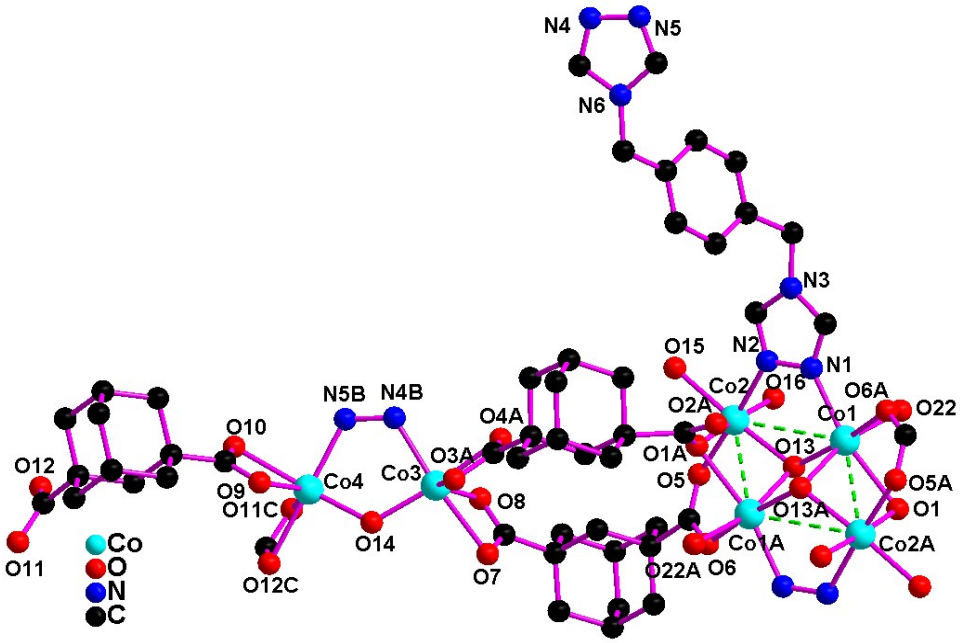


Fig. S1. The coordination environment of the tetranuclear cobalt(II) [$Co_4(\mu_3\text{-}OH)_2$] and binuclear cobalt(II) [$Co_2(\mu_2\text{-}OH)$] in **1**. Symmetry codes: A -x, -y+1, -z; B -x+1, -y+1, -z+1; C -x, -y-1, -z+1; D x, y-1, z; E -x, -y, -z+1; F x, y+1, z.

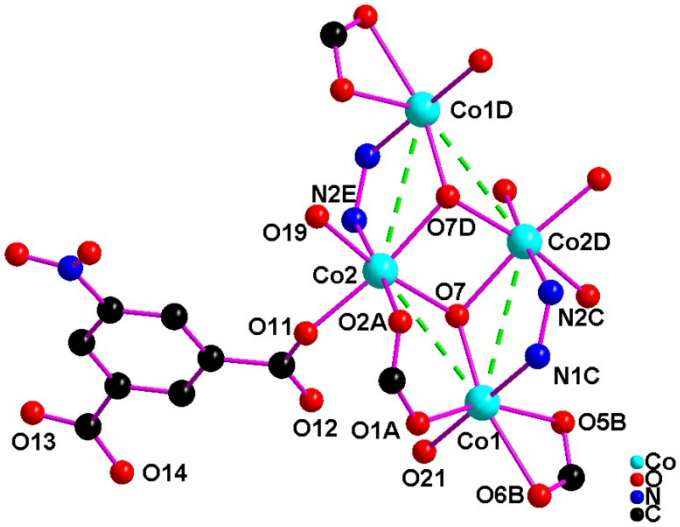


Fig. S2. The first kind of tetranuclear cobalt(II) cluster in **2**. Symmetry codes: A 1-x, 2-y, 2-z; B x, y, 1+z; C -1+x, 1+y, 1+z; D 1-x, 2-y, 3-z; E 2-x, 1-y, 2-z; F 1-x, 1-y, 2-z; G x, y, -1+z; H 1+x, -1+y, -1+z.

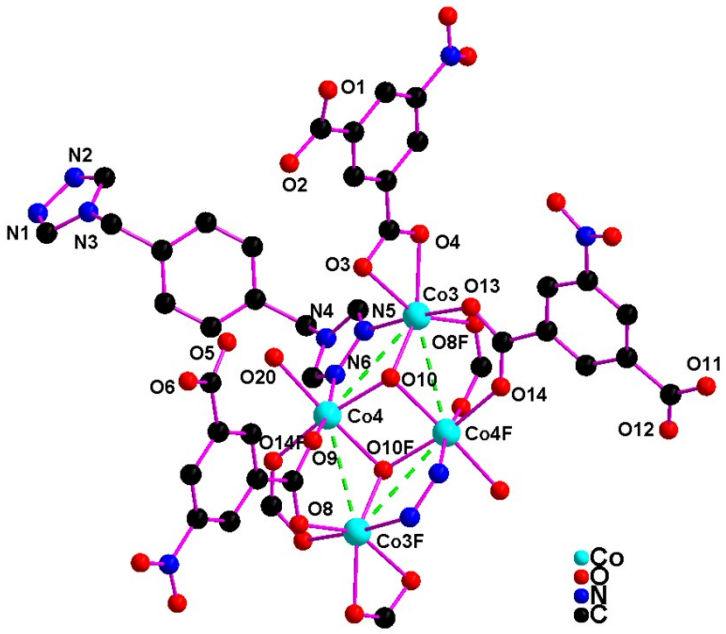


Fig. S3. The second kind of the tetranuclear cobalt(II) cluster in **2**.

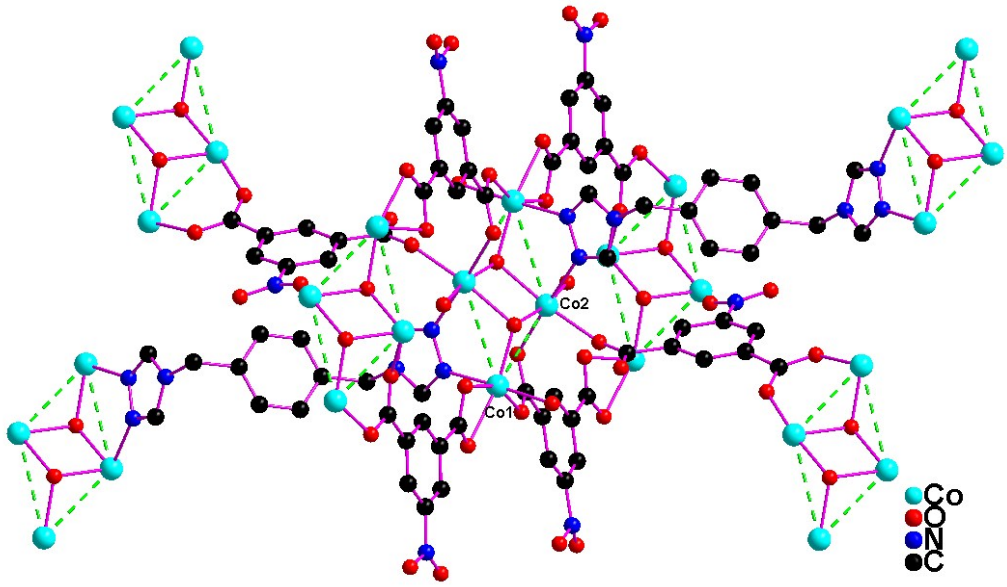


Fig. S4. The first kind of tetranuclear unit connects six tetranuclear units in **2**.

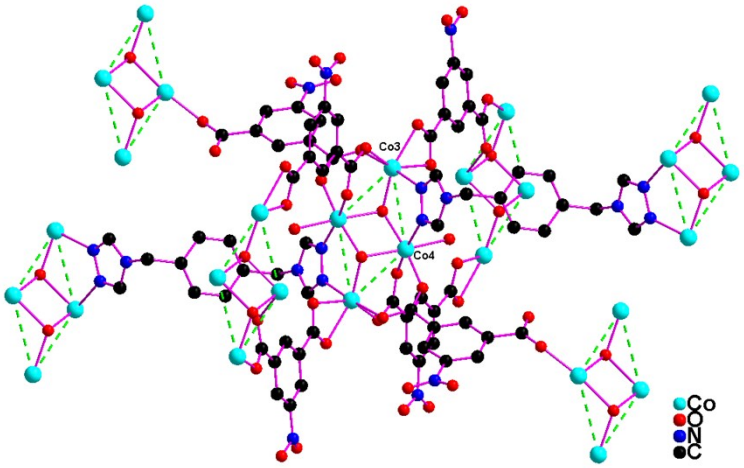


Fig. S5. The second kind of tetranuclear unit connects six tetranuclear units in **2**.

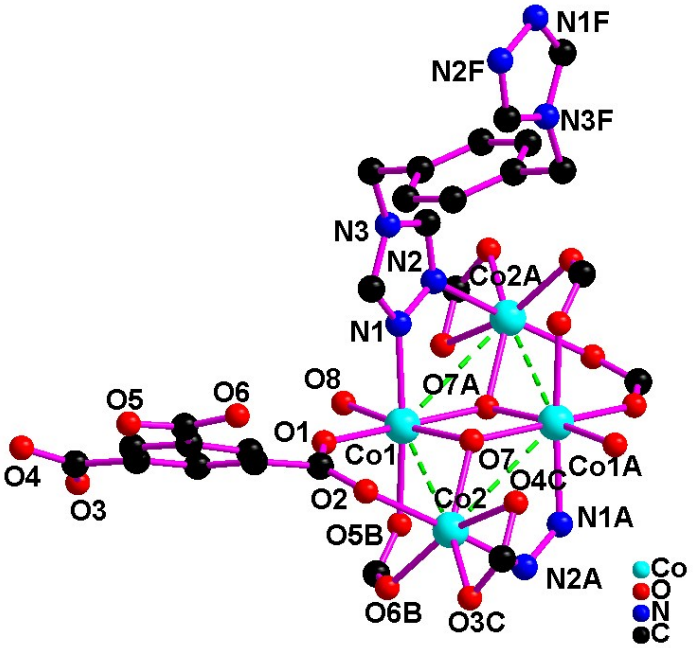


Fig. S6. The coordination environment of the tetranuclear cobalt(II) cluster in **3**. Symmetry codes: A -x, -y+1, -z+1; B x-1/2, -y+1/2, z-1/2; C x+1/2, -y+1/2, z-1/2; D x-1/2, -y+1/2, z+1/2; E x+1/2, -y+1/2, z+1/2; F -x+1, -y+1, -z+2; G -x+1/2, y+1/2, -z+3/2; H -x-1/2, y+1/2, -z+3/2; I 1+x, y, 1+z.

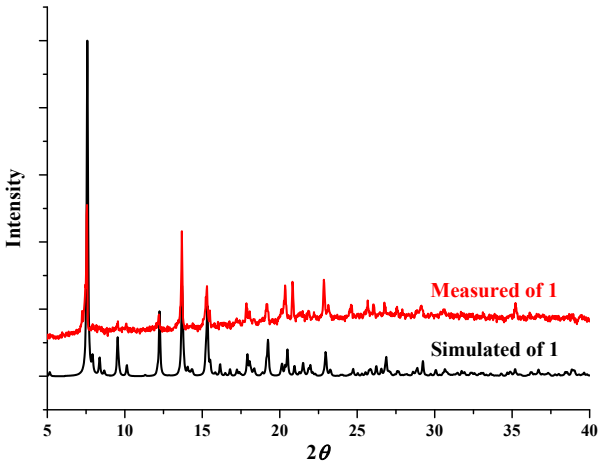


Fig. S7. PXRD patterns of compound **1**.

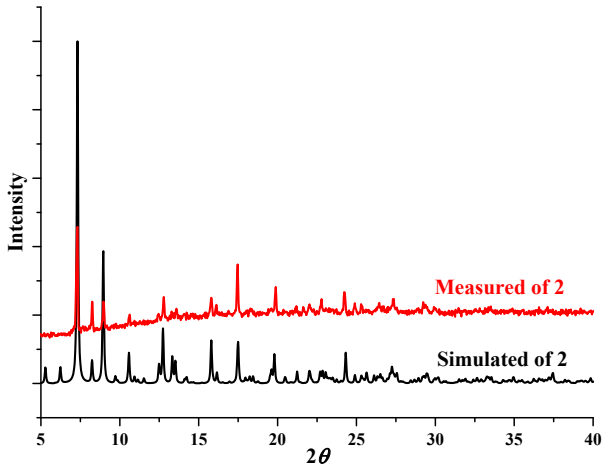


Fig. S8. PXRD patterns of compound **2**.

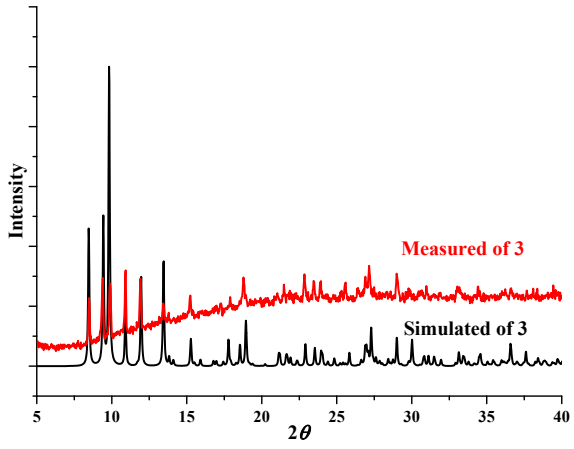


Fig. S9. PXRD patterns of compound **3**.

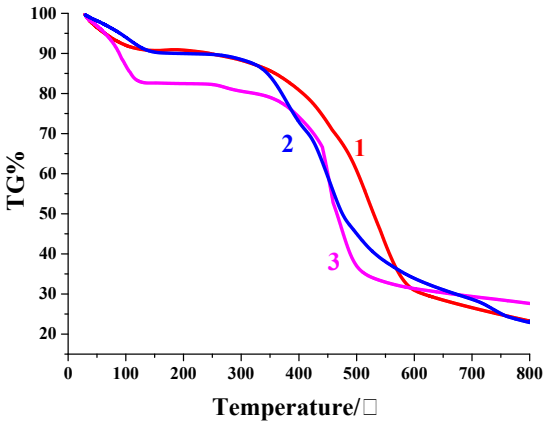


Fig. S10. TG vs Temperature curve of **1**-**3**.