Supporting Information

Metal-responsive activation of C-O and C-C bonds of an aromatic vicinal diol in hydrothermal conditions: synthesis, structure, mechanism and magnetic properties

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1. Crystallography

Mo-*Kα* radiation ($\lambda = 0.71073$ Å)

The data of the complexes **1** and **6** were collected on a Bruker Smart Apex II diffractometer equipped with 1 K CCD instrument by using a graphite monochromator utilizing Mo-*Kα* radiation at room temperature.

Single-crystal X-ray diffraction data collection of complexes **2** and **4** were performed on an Oxford Supernova diffractometer at 123(2) K with graphite-monochromated Mo-*Kα* radiation using the *ω*-scan technique.

The structures of **1**, **2**, **4** and **6** were solved by direct methods with the program package[1, 2], and absorption corrections were made via SADABS. Cell parameters were determined using SMART software.

Synchrotron radiation ($\lambda = 0.72000$ Å)

Single-crystal X-ray diffraction data for complexes **3** and **7** were collected in Beijing Synchrotron Radiation Facility (BSRF) beamline 3W1A which mounted with a MARCCD-165 detector with storage ring working at 2.5 GeV. In the process, the crystals were protected by liquid nitrogen at 100(2) K. Data were collected by the program marccd and processed using HKL2000[3-5]. For the synchrotron data, DISP instructions were used for the absorption coefficient of each element.

All data reduction and corrections were performed using SAINTPlus. Structures were solved by direct methods with the program SHELXS-97 and refined by full-matrix least-squares methods on all F^2 data with SHELXL-2014. Non-H atoms were refined anisotropically. H atoms attached to C and N atoms of all complexes were placed in geometrically idealized positions, with Csp^2-H = 0.93, and Nsp^3-H = 0.86 Å and refined with $U_{iso}(H) = 1.2U_{eq}(C$ or $N)$. H atoms attached to O were located from difference Fourier maps and refined as riding in their as-found positions with $U_{iso}(H) = 1.5U_{eq}(O)$ for 100% occupancy and $U_{iso}(H) = 1.0U_{eq}(O)$ for partial occupancy. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. Crystallographic data of complexes are shown in Table S1. The CIF files deposited in the Cambridge Crystallographic Data Center (CCDC reference numbers 1016036-1016041) can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html; or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K. [fax: (t44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

The complexes characterized by $[M_5L_6]^{4+}$ cluster (**1-4**) almost feature large voids, which may derive from two aspects. The one is from the triple-helix cavity buried in the cluster, which is about a void of 54 Å^3 in each cluster. That is about 200-400 Å^3 void in each cell, based on the Z value. Combined with our studies[6, 7], we speculate that these voids are inherent and there is a indeed cavity without any content in it for each molecule. The other is from disordered anions and solvent molecules. So the data were corrected for disordered electron density through use of the SQUEEZE[8] procedure in PLATON. To verify the possible electron contents of the large voids, the methods of EA, ICP and TGA were used. Comments about each complex were added seriatim.

In **1**, RIGU instruction was employed to have ellipsoids of sites (N16, C13, C27, C38, C44, C54, C56, C61 and C87) been restraint to more appropriate values. The formula in the left column of checkcif was $C_{96}H_{66}Co_5N_{24}O_6$, which represented $[Co_5(H_2L)_6]^{4+}$, and did not contain the contribution of the anions and solvent molecule. Further, the checkcif report indicated that structure contains very large solvent accessible voids. Data were corrected for disordered electron density through use of the *PLATON* SQUEEZE procedure, and the major _platon_squeeze_void_volume was 2240 $Å^3$ and electrons of 548. According to EA and TGA results, each asymmetric unit contains one and a half nitrate, two and a half hydroxy and one and a half water molecules as the counter ions and solvents of crystallization (Fig. S7). They contain 84 electrons. Z value is equal to 4, so there are 336 electrons in this void. The other electrons of 212 are corresponding to about 5.3 water molecules in each asymmetric unit, but without any experimental evidence. They might be lost before performing the EA and TGA experiments or there might be an indeed cavity without any content existing, such as the triple-helix cavity buried in the M_5O_6 cluster. The details were inserted in _platon_squeeze_details text of the CIF. These results matched with the formula $C_{96}H_{71.5}Co_5N_{25.5}O_{14.5}$, corresponding to $[Co_5(H_2L)_6]\cdot(NO_3)_{1.5}\cdot(OH)_{2.5}\cdot1.5H_2O$.

In **2**, ISOR and RIGU instructions were employed to have ellipsoids of sites (C67, C87, C99, Br6 and Br8) and (N25, N26, C13, C69, C97, C98, C100, C102, O7, O8,) respectively been restraint to more appropriate values. Four reflections with (Iobs-Icalc)/SigmaW > 10 Outliers were omitted. The C-N and C-O distances of two DMF solvent molecules were restrained to reasonable ranges. 68 restraints were used for refinement anisotropically. The formula in the left column of checkcif was $C_{102}H_{80}Br_4Co_5N_{26}O_8$, which represented $[Co_5(H_2L)_6]\cdot2(C_3H_7NO)\cdot Br_4$, and did not contain the contribution of the disordered solvent molecule. Further, the checkcif report indicated that structure contains very large solvent accessible voids. Data were corrected for disordered electron density through use of the SQUEEZE option in PLATON, and the two _platon_squeeze_void_volume add up to 9206 $Å^3$ and electrons of 3444. According to EA and TGA results, each asymmetric unit contains three and a

half water molecules as solvents of crystallization (Fig. S8). They contain 35 electrons. Z value is equal to 8, so there are 280 electrons in this void. The other electrons of 3164 can't be identified because of the lack of experimental evidence. Attempts to refine peaks of residual electron density as solvent molecules were unsuccessful. They might be some other solvent molecules like DMF and water molecules lost before performing the EA and TGA experiments or there might be indeed not any content existing. The details were inserted in _platon_squeeze_details text of the CIF. These results matched with the formula $C_{102}H_{87}Br_4Co_5N_{26}O_{11.5}$, corresponding to $[Co_5(H_2L)_6] \cdot 2(C_3H_7NO) \cdot Br_4 \cdot 3.5H_2O$.

Compared to the other complexes of $[Co_5L_6]^{4+}$ or $[Ni_5L_6]^{4+}$ systems, the complex **2** seemed to have the largest voids. It may because that the crystal was obtained from the recrystallization in DMF, and the space group of crystallography was changed. It belonged to $C2/c$ space group, but all other similar $[Co_5L_6]^{4+}$ or $[Ni_5L_6]^{4+}$ systems belonged to $P2_1/c$ (or $P2_1/n$). It had about twice the cell content as **1** or **3**, and its cell volume was about three times larger. Thus, the largest cell voids existed in complex **2** for all the $[M_5L_6]^{4+}$ systems.

In **3**, ISOR instruction was employed to have ellipsoids of sites (N21, N22, N24, C12, C22, C28, C29, C44-C48, C51-C54, C63, C67-C72, C79, C82-C89 and C95) been restraint to more appropriate values. 198 restraints were used for refinement anisotropically.

The formula in the left column of checkcif was $C_{96}H_{66}Co_5N_{24}O_6$, which represented $[Co_5(H_2L)_6]^{4+}$, and did not contain the contribution of the anions and solvent molecule. Further, the checkcif report indicated that structure contains very large solvent accessible voids. Data were corrected for disordered electron density through use of the *PLATON* SQUEEZE procedure, and the major _platon_squeeze_void_volume was 2142 $Å^3$ and electrons of 563. According to EA and TGA results, each asymmetric unit contains one chloridion, two hydroxyl, one formate and two water molecules as the counter ions and solvents of crystallization (Fig. S9). They contain 78 electrons. Z value is equal to 4, so there are 312 electrons in this void. The other electrons of 251 are corresponding to about 6.3 water molecules in each asymmetric unit, but without any

experimental evidence. They might be lost before performing the EA and TGA experiments or there might be indeed not any content existing. The details were inserted in _platon_squeeze_details text of the CIF. These results matched with the formula $C_{97}H_{73}N_{24}Co_5O_{12}Cl$, corresponding to $[Co_5(H_2L)_6]Cl\cdot(OH)_2\cdot(HCOO)\cdot2H_2O$.

In **4**, ISOR and RIGU instructions were employed to have ellipsoids of sites (C8, C15, C22, C27, C33, C35, C47, C60, C62, C63, C64, C77, C93, C94, C95, Cl1, Cl2, Cl3 and Cl4) and (C37, C38 and C39) respectively been restraint to more appropriate values. 123 restraints were used for refinement anisotropically. The formula in the left column of checkcif was $C_{96}H_{66}Cl_4Fe_2N_{24}O_6Zn_3$, which represented $[Fe_2Zn_3(H_2L)_6]Cl_4$, and did not contain the contribution of the disordered solvent molecule. Further, the checkcif report indicated that structure contains large solvent accessible voids. Data were corrected for disordered electron density through use of the SQUEEZE procedure in PLATON, and the two major _platon_squeeze_void_volume add up to 1374 $Å^3$ and electrons of 522. According to EA and TGA results, each asymmetric unit contains three water molecules as solvents of crystallization (Fig. S10). They contain 30 electrons. Z value is equal to 4, so there are 120 electrons in this void. The other electrons of 402 are corresponding to about 10 water molecules in each asymmetric unit, but without any experimental evidence. They might be lost before performing the EA, ICP and TGA experiments or there might be indeed not any content existing. The details were inserted in _platon_squeeze_details text of the CIF. These results matched with the formula $C_{96}H_{72}Cl_4Fe_{1.15}N_{24}O_9Zn_{3.85}$, corresponding to $[Fe_{1.15}Zn_{3.85}(H_2L)_6]Cl_4\cdot3H_2O$.

In **6**, DELU and ISOR instructions were employed to have ellipsoids of sites (C10, C11, C20, C29, C30-C37, N4, N8-N10) and (C12, C18, C19, C26, C27, Br3 and Br4) been restraint to more appropriate values. 56 restraints were used for refinement anisotropically. The formula in the left column of checkcif was $C_{37}H_{35}Br_4ClCuN_{10}$, which represented $[(C_7H_6N_2)_4Cu^{II}Br](C_9H_{11}N_2)\cdot Cl\cdot3Br$, and did not contain the contribution of the disordered solvent molecule. Further, the checkcif report indicated that structure contains large solvent accessible voids. Data were corrected for disordered electron density through use of the SQUEEZE procedure in PLATON, and

the _platon_squeeze_void_volume was 638 $Å^3$ and electrons of 247. According to EA result and the pH value of the mother solution between 1 and 2, each asymmetric unit contains two hydrated cations. They contain 22 electrons. Z value is equal to 2, so there are 44 electrons in this void. The other electrons of 203 are corresponding to about 10 water molecules in each asymmetric unit, but without any experimental evidence. They might be lost before performing the EA experiment or there might be indeed not any content existing. The details were inserted in _platon_squeeze_details text of the CIF. These results matched with the formula $C_{37}H_{41}Br_4ClCuN_{10}O_2$, corresponding to $[(C_7H_6N_2)_4Cu^{II}Br]\cdot 2H_3O\cdot(C_9H_{11}N_2)\cdot Cl\cdot 3Br$.

In **7**, ISOR instruction was employed to have ellipsoids of site O2 been restraint to more appropriate value. Two reflections with (Iobs-Icalc)/SigmaW > 10 Outliers were omitted. There were disorder and partially occupied sites O2 and O3 in the counterion of NO_3^-. 6 restraints were used for refinement anisotropically. The formula in the left column of checkcif was $C_{56}H_{48}ClCu_2N_{18}O_6$, which represented $[(C_7H_6N_2)_8Cu^{II}_2Cl]\cdot(NO_3)_2$. Further, the checkcif report indicated that structure contains large solvent accessible voids. Data were corrected for disordered electron density through use of the SQUEEZE option in PLATON, and the four major _platon_squeeze_void_volume add up to 480 $Å^3$ and electrons of 152. According to EA results, each asymmetric unit contains a formate ion as the counter ion of crystallization. They contain 23 electrons. Z value is equal to 4, so there are 92 electrons in this void. The other electrons of 60 are corresponding to about one and a half water molecules in each asymmetric unit, but without any experimental evidence. They might be lost before performing the EA experiment or there might be indeed not any content existing. The details were inserted in _platon_squeeze_details text of the CIF. These results matched with the formula $C_{57}H_{49}ClCu_2N_{18}O_8$, corresponding to $[(C_7H_6N_2)_8Cu^{II}_2Cl]\cdot(HCOO)\cdot(NO_3)_2$.

2. Supporting Tables and Figures

Figure S1. The structure of compound **11** containing in **6**. Displacement ellipsoids are drawn at the 10% probability level and H atoms are shown as small spheres of arbitrary radii.

Figure S2. The XPRD patterns of experimental (blue) and simulation (black) in RT for complex **1**.

Figure S3. The XPRD patterns of experimental (blue) and simulation (black) in RT for complex **2**.

Figure S4. The XPRD patterns of experimental (blue) and simulation (black) in RT for complex **3**.

Figure S5. The XPRD patterns of experimental (blue) and simulation (black) in RT for complex **4**.

Figure S6. The XPRD patterns of experimental in RT for the complex **5**.

Figure S7. TG spectrum of complex **1**, solvent molecules and counter anions loss of 7.9% (calcd: 7.7%).

Figure S8. TG spectrum of complex **2**, seven water and four DMF molecules loss of 8.8% (calcd: 8.4%).

Figure S9. TG spectrum of complex **3**. The loss of 3.1% can be attributed to the removal of two waters and two hydroxyls (calcd: 3.3%), and the second weight loss of

7.3% at the inflexion 358ºC corresponds to the formate and chlorine anions (calcd: 7.2%).

Figure S10. TG spectrum of complex **4**. The loss of 1.8% can be attributed to the removal of two waters molecules (calcd: 1.7%), and the second weight loss of 9.0% at the inflexion 436ºC corresponds to three waters molecules and four chlorine anions (calcd: 9.1%).

Figure S11. Plot of χ_m^{-1} ($\square$) and $\chi_m T$ (Δ) *vs* T and field dependence of magnetization at 2K (inset) for complex **2**.

Figure S12. Plot of χ_m^{-1} ($\square$) and $\chi_m T$ (Δ) *vs* T for complex **3**.

Figure S13. Plot of χ_m^{-1} ($\square$) and $\chi_m T$ (Δ) *vs* T for complex **4**.

Table S1 Crystal data and structure refinements for **1–4**, **6** and **7**.

Compound	1	2	3	4	6	7
Formula	$C_{96}H_{71.5}Co_5N_{25.5}O_{14.5}$	$C_{102}H_{87}Br_4Co_5N_{26}O_{11.5}$	$C_{97}H_{73}ClCo_5N_{24}O_{12}$	$C_{96}H_{72}Cl_4Fe_2N_{24}O_9Zn_3$	$C_{37}H_{41}Br_4ClCuN_{10}O_2$	$C_{57}H_{49}ClCu_2N_{18}O_8$
Fw	2108.93	2475.26	2096.89	2155.38	1076.43	1276.67
Radiation type	Mo-Kα	Mo-Kα	synchrotron	Mo-Kα	Mo-Kα	Synchrotron
T/K	298 (2)	123(2)	100(2)	123(2)	293(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	tetragonal
Space group	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1/c$	P-1	$P4/ncc$
a/Å	13.5550(14)	41.0956(15)	13.241(3)	12.9691(11)	10.9907(11)	15.327(3)
b/Å	26.637(3)	24.8982(9)	26.889(5)	26.539(2)	14.3055(15)	15.327(3)
c/Å	28.386(3)	28.2361(11)	28.423(6)	29.040(2)	18.0914(19)	25.887(5)
α/°	90	90	90	90	72.806(6)	90.00
β/°	99.374(2)	104.629(2)	101.13(3)	104.905(7)	87.022(6)	90.00
γ/°	90	90	90	90	72.711(6)	90.00
V/Å^3	10112.4(18)	27954.7(18)	9929(4)	9658.9(13)	2592.6(5)	6081(3)
Z	4	8	4	4	2	4
D_{calcd}/mg m^{-3}	1.385	1.176	1.403	1.482	1.379	1.394
μ/mm^{-1}	0.877	1.779	0.944	1.209	3.593	0.811
$R_1{}^a$ [$I>2\sigma(I)$]	0.0637	0.1100	0.0693	0.1192	0.1057	0.1543
$wR_2{}^a$ (all data)	0.1641	0.3578	0.2236	0.3849	0.3193	0.3501

a

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

Co1—N5	2.083(6)	Co1—O3	2.195(4)
Co1—N9	2.089(5)	Co1—O1	2.191(4)
Co1—N1	2.104(5)	Co1—O2	2.204(4)
Co2—N17	2.067(6)	Co2—O4	2.174(4)

Co2—N13	2.081(6)	Co2—O6	2.187(4)
Co2—N21	2.099(5)	Co2—O5	2.187(4)
Co3—N3	1.979(5)	Co3—O4	1.982(4)
Co3—N15	1.991(6)	Co3—O1	1.986(4)
Co4—N7	1.954(6)	Co4—O5	1.996(4)
Co4—N19	1.984(5)	Co4—O2	2.007(4)
Co5—N23	2.002(5)	Co5—O6	1.980(4)
Co5—N11	1.985(5)	Co5—O3	1.989(4)
Co1···Co2	5.4728(13)	Co1···Co3	3.6374(13)
Co1···Co4	3.6468(12)	Co1···Co5	3.6491(13)
Co2···Co3	3.5777(12)	Co2···Co4	3.6313(14)
Co2···Co5	3.6071(12)	Co3···Co4	3.9297(13)
Co4···Co5	4.2234(14)	Co3···Co5	4.1839(12)
Co3—O4—Co2	118.8(2)	Co4—O2—Co1	119.9(2)
Co3—O1—Co1	120.99(19)	Co4—O5—Co2	120.4(2)
Co5—O3—Co1	121.38(18)	Co5—O6—Co2	119.8(2)

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

Co1—N1	2.051(7)	Co1—O2	2.136(6)
Co1—N9	2.057(7)	Co1—O1	2.154(5)
Co1—N5	2.063(7)	Co1—O3	2.167(5)
Co2—N21	2.052(8)	Co2—O6	2.121(5)
Co2—N17	2.036(7)	Co2—O4	2.138(6)
Co2—N13	2.092(7)	Co2—O5	2.158(6)
Co3—N15	1.950(7)	Co3—O1	1.958(5)
Co3—N3	1.968(7)	Co3—O4	1.958(5)
Co4—N19	1.961(8)	Co4—O5	1.979(5)
Co4—N7	1.960(7)	Co4—O2	1.994(5)
Co5—N23	1.973(8)	Co5—O3	1.969(6)
Co5—N11	1.986(7)	Co5—O6	1.989(6)
Co1···Co2	5.4326(16)	Co1···Co3	3.5852(17)
Co1···Co4	3.5857(18)	Co1···Co5	3.6013(16)
Co2···Co3	3.5550(17)	Co2···Co4	3.6123(15)
Co2···Co5	3.5588(18)	Co3···Co4	4.2083(17)
Co4···Co5	3.8740(17)	Co3···Co5	4.0363(19)
Co3—O1—Co1	121.3(3)	Co3—O4—Co2	120.3(3)
Co4—O2—Co1	120.5(3)	Co4—O5—Co2	121.6(3)
Co5—O3—Co1	121.0(3)	Co5—O6—Co2	119.9(3)

Table S4 Selected bond lengths (Å) and angles (°) for **3**

Co1—N1	2.092(3)	Co1—O3	2.188(3)
Co1—N9	2.062(3)	Co1—O1	2.185(3)
Co1—N5	2.094(3)	Co1—O2	2.169(3)
Co2—N17	2.052(6)	Co2—O4	2.162(3)
Co2—N21	2.068(5)	Co2—O6	2.194(4)
Co2—N13	2.088(5)	Co2—O5	2.154(3)
Co3—N3	1.972(5)	Co3—O1	1.969(3)
Co3—N15	1.979(4)	Co3—O4	1.960(4)

Co4—N7	1.977(4)	Co4—O5	1.970(3)
Co4—N19	1.965(4)	Co4—O2	1.974(3)
Co5—N23	1.973(5)	Co5—O6	1.964(3)
Co5—N11	1.982(4)	Co5—O3	1.957(3)
Co1···Co2	5.4713(14)	Co1···Co3	3.6040(11)
Co1···Co4	3.5965(10)	Co1···Co5	3.6015(11)
Co2···Co3	3.5727(15)	Co2···Co4	3.5829(15)
Co2···Co5	3.5753(13)	Co3···Co4	4.0966(14)
Co4···Co5	3.8544(11)	Co3···Co5	4.1046(12)
Co5—O3—Co1	120.54(13)	Co4—O5—Co2	120.60(17)
Co3—O4—Co2	120.08(15)	Co4—O2—Co1	120.39(14)
Co3—O1—Co1	120.31(14)	Co5—O6—Co2	118.49(17)

Table S5 Selected bond lengths (Å) and angles (°) for **4** (M_5L_6, M_5= $Fe_{1.15}Zn_{3.85}$)

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M1—N1	2.030(11)	M1—O2	2.164(8)
M1—N5	2.065(11)	M1—O1	2.193(8)
M1—N9	2.071(11)	M1—O3	2.190(9)
M2—N21	2.052(9)	M2—O5	2.194(9)
M2—N17	2.068(10)	M2—O4	2.195(7)
M2—N13	2.084(10)	M2—O6	2.215(8)
M3—N15	1.954(11)	M3—O4	1.970(8)
M3—N3	1.969(11)	M3—O1	1.966(8)
M4—N7	1.976(10)	M4—O2	1.976(8)
M4—N19	1.986(10)	M4—O5	1.964(8)
M5—N11	1.960(10)	M5—O6	1.956(7)
M5—N23	1.942(10)	M5—O3	1.969(8)
M1···M2	5.5084(22)	M1···M3	3.6421(22)
M1···M4	3.5855(24)	M1···M5	3.5854(24)
M2···M3	3.6508(24)	M2···M4	3.6249(21)
M2···M5	3.6279(19)	M3···M4	4.1532(25)
M4···M5	4.1156(23)	M3···M5	3.9182(22)
M3—O1—M1	122.1(4)	M3—O4—M2	122.3(4)
M4—O2—M1	120.0(4)	M4—O5—M2	121.2(4)
M5—O3—M1	119.0(4)	M5—O6—M2	120.8(4)
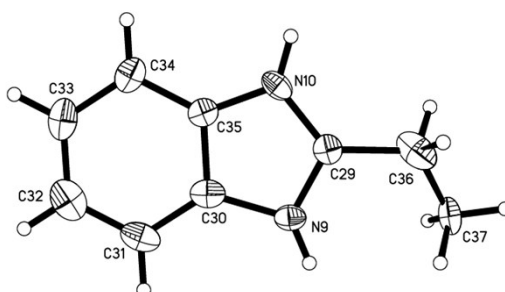
Figure S1 The structure of compound **11** containing in **6**. Displacement ellipsoids are drawn at the 10% probability level and H atoms are shown as small spheres of arbitrary radii.

Table S6 Crystal data and structure refinements for **8**.

Compound	**8**
Formula	$C_{32}H_{36}Cl_6Cu_4N_8O_3$
Fw	1047.55
Radiation type	Mo-Kα
T/K	298(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.9982(9)
b/Å	13.2250(9)
c/Å	13.8680(10)
α/°	68.0970(10)
β/°	74.3680(10)
γ/°	71.4490(10)
V/Å^3	2065.9(3)
Z	2
D_{calcd}/mg m^{-3}	1.684
μ/mm^{-1}	2.462
$R_1{}^a$ [$I>2\sigma(I)$]	0.0415
$wR_2{}^a$ (all data)	0.1015

$$_a R_1 = \sum \left||F_0| - |F_c|\right| / \sum |F_0|; \; wR_2 = \left[\sum w\left(F_0 - F_c{}^2\right)^2 / \sum w\left(F_0{}^2\right)^2\right.$$

The structure of compound **8** has been reported by Zhang[34], and this is available in the CSD as REFCODE SUCXOD01. The unit-cell data reported in Table S6 are from the independent work by us and its CIF is available in the Supplementary material file for this submission.

Table S7. Synthesis conditions and product types between 3d ions and TDB.

3d ions	Synthesis condition	Product type	Ligand	Remark
Co^{2+}	NTP	Mononuclear	TDB	Ref[9]
Ni^{2+}, Cu^{2+}	NPT	Mononuclear	TDB	Ref[10]
Cu^{2+}	NPT	Tetranuclear	TDB	Ref[11, 12]
Zn^{2+}	80°C, normal pressure	Tetranuclear	TDB	Ref[9]
Co^{2+}	100°C, solvothermal	Co$_{16}$	TDB	Ref[13]
Co^{2+}, Ni^{2+}	140°C, solvothermal	Pentanuclear	H$_3$L	Ref[9]
Ni^{2+}	175°C, hydrothermal	Pentanuclear	H$_3$L	Ref[10]

NPT = normal pressure and temperature

Table S8. DFT calculation results of the binding energies of the $[TM_5(H_2L)_6]^{4+}$ systems.

TM ions	Total energy of $[TM_5(H_2L)_6]^{4+}$ (Hartree)	Spin multiplicity (S)	Energy of TM^{2+} (Hartree)	Energy of $(H_2L)^-$ (Hartree)	Binding energy (Kcal/mol)
Mn^{2+}	-11197.12861340	26	-1150.0232810	-907.156293	-2556.7
Fe^{2+}	-11760.45614320	21	-1262.6435539	-907.156293	-2698.6
Co^{2+}	-12355.61574160	16	-1381.6420922	-907.156293	-2803.3
Ni^{2+}	-12983.17549520	11	-1507.1043131	-907.156293	-2959.3
Cu^{2+}	-13643.72335440	6	-1639.2130839	-907.156293	-2961.9
Zn^{2+}	-14338.06888190	1	-1778.1070143	-907.156293	-2884.0

Binding energy = $E([TM_5(H_2L)_6]^{4+})$ - 5 × $E(TM^{2+})$ - 6 × $E((H_2L)^-)$

1 Hartree = 2565.5 KJ/mol = 627.5094 Kcal/mol
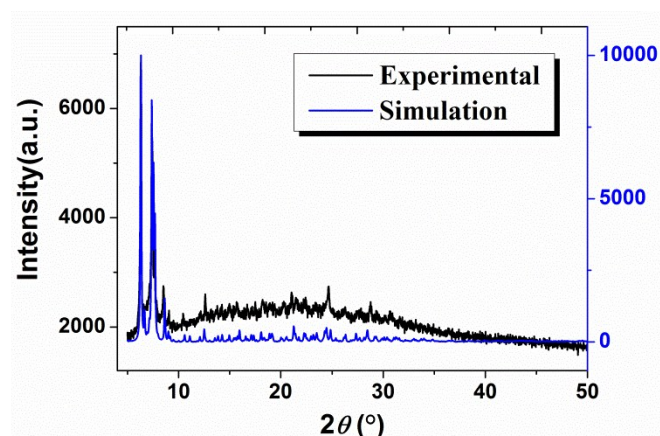
Figure S2. The XPRD patterns of experimental (blue) and simulation (black) in RT for complex **1**.
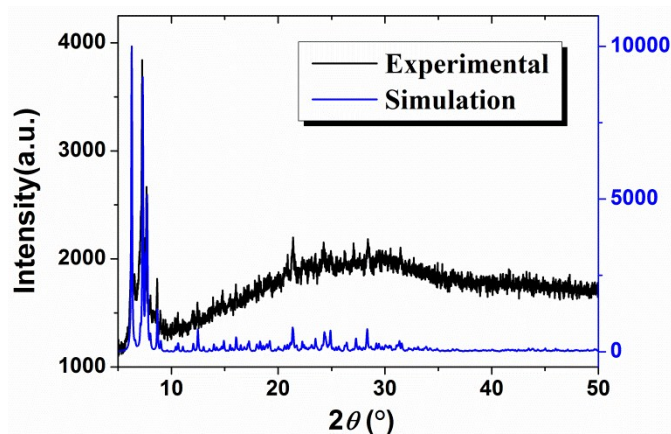
Figure S3. The XPRD patterns of experimental (blue) and simulation (black) in RT for complex **2**.

Figure S4. The XPRD patterns of experimental (blue) and simulation (black) in RT for complex **3**.
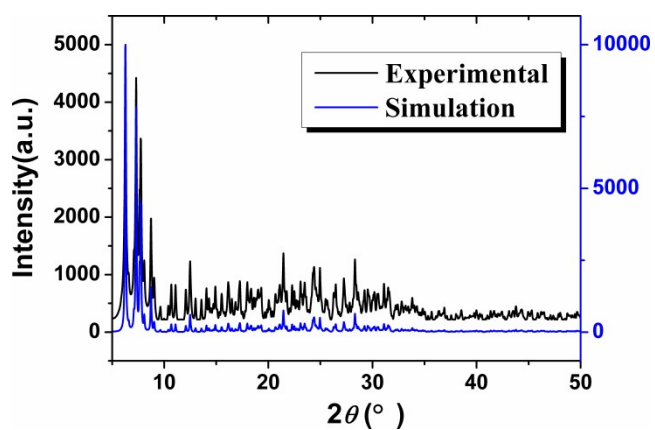
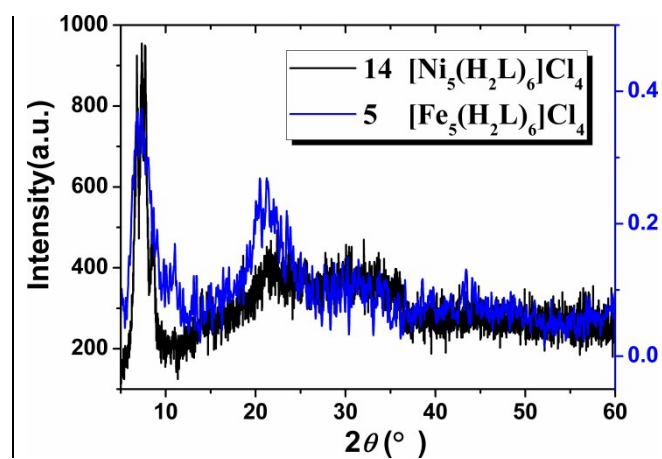**Figure S5**. The XPRD patterns of experimental (blue) and simulation (black) in RT for complex **4**.

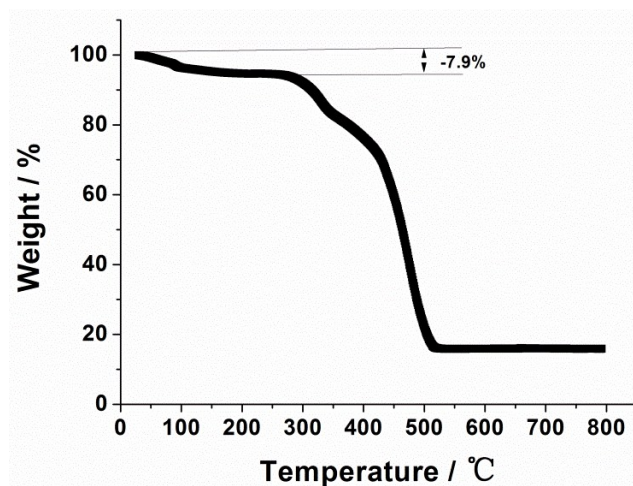**Figure S6**. The XPRD patterns of experimental in RT for the complex **5**.

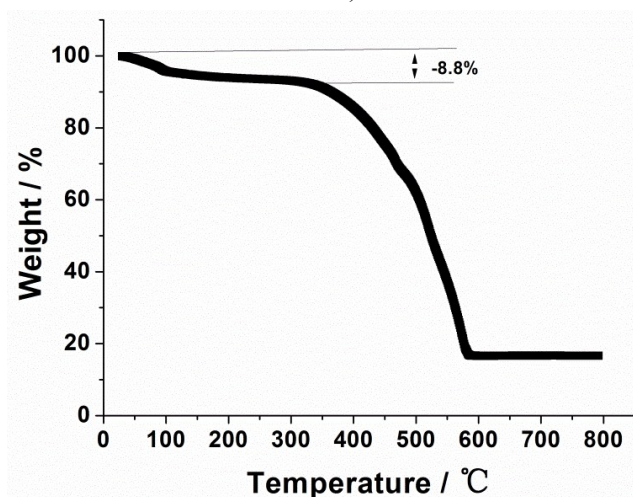**Figure S7**. TG spectrum of complex **1**, solvent molecules and counter anions loss of 7.9% (calcd: 7.7%).

Figure S8. TG spectrum of complex **2**, three and a half water and two DMF molecules loss of 8.8% (calcd: 8.4%).
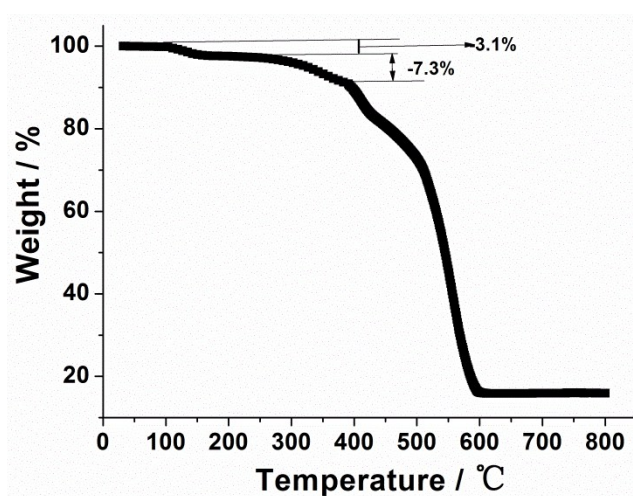
Figure S9. TG spectrum of complex **3**. The loss of 3.1% can be attributed to the removal of two waters and two hydroxyls (calcd: 3.3%), and the second weight loss of 7.3% at the inflexion 358ºC corresponds to the formate and chlorine anions (calcd: 7.2%).
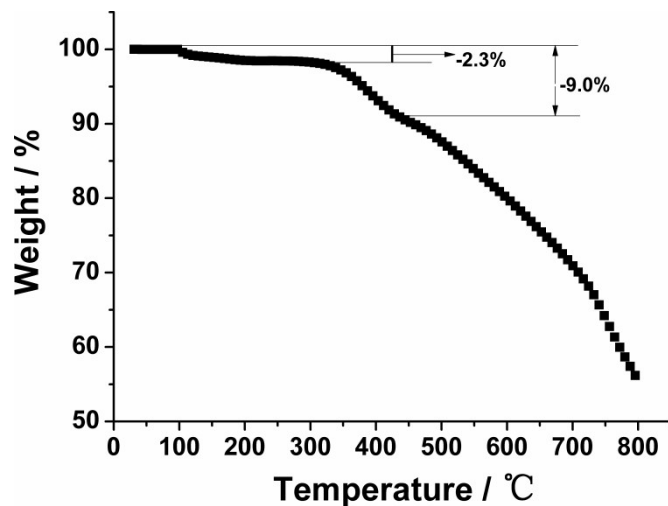
Figure S10. TG spectrum of complex **4**. The loss of 2.3% can be attributed to the removal of three waters molecules (calcd: 2.5%), and the second weight loss of 9.0% at the inflexion 436ºC corresponds to four chlorine anions (calcd: 9.1%).
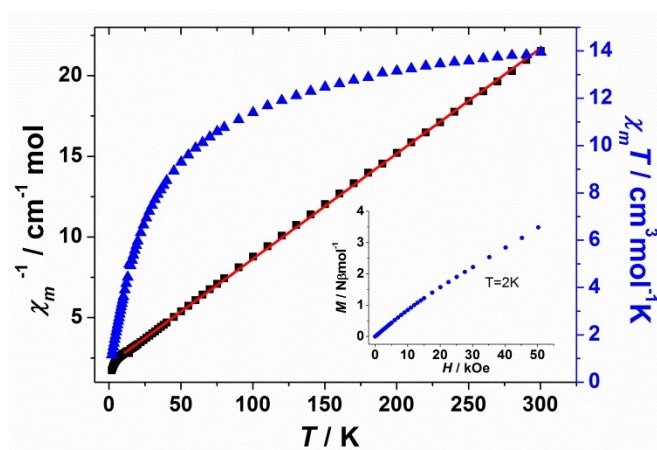

Figure S11. Plot of χ_m^{-1} (□) and $\chi_m T$ (Δ) *vs* T and field dependence of magnetization at 2K (inset) for complex **2**.
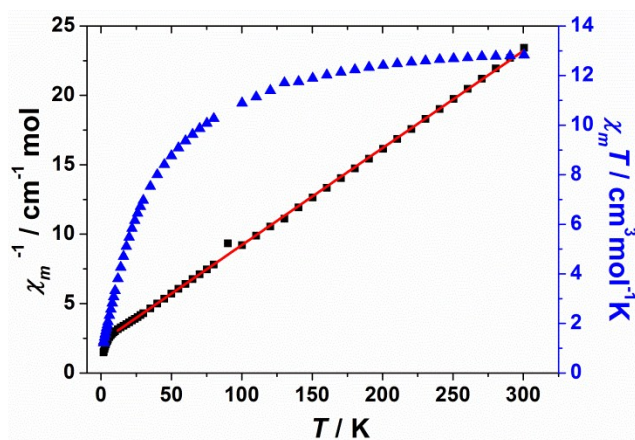

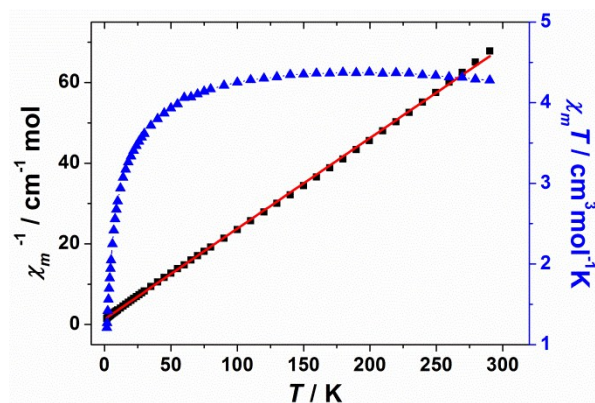**Figure S12**. Plot of χ_m^{-1} (□) and $\chi_m T$ (Δ) *vs* T for complex **3**.

Figure S13. Plot of χ_m^{-1} (□) and $\chi_m T$ (Δ) *vs* T for complex **4**.

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