Electronic Supplementary Information

Five Transitional Metal Coordination Polymers Driven by a Semirigid Trifunctional Nicotinic Acid Ligand: Selective Adsorption and Magnetic Properties

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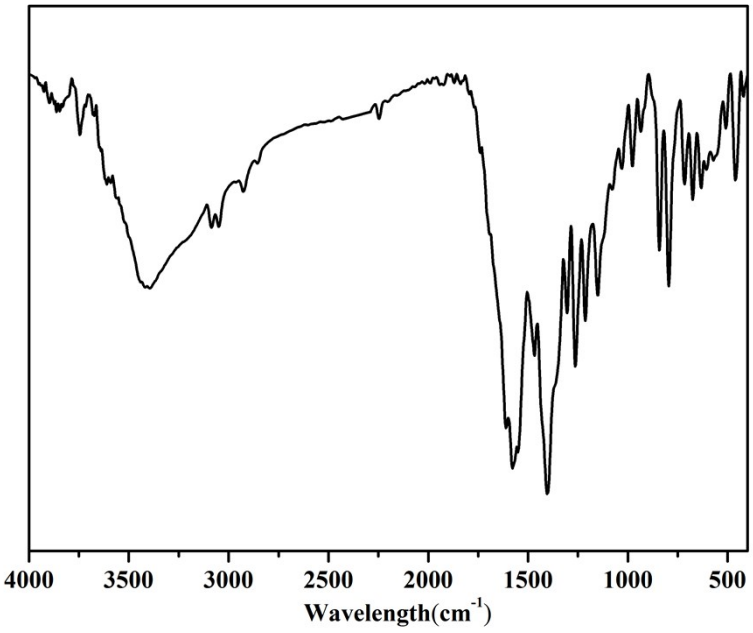
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3500
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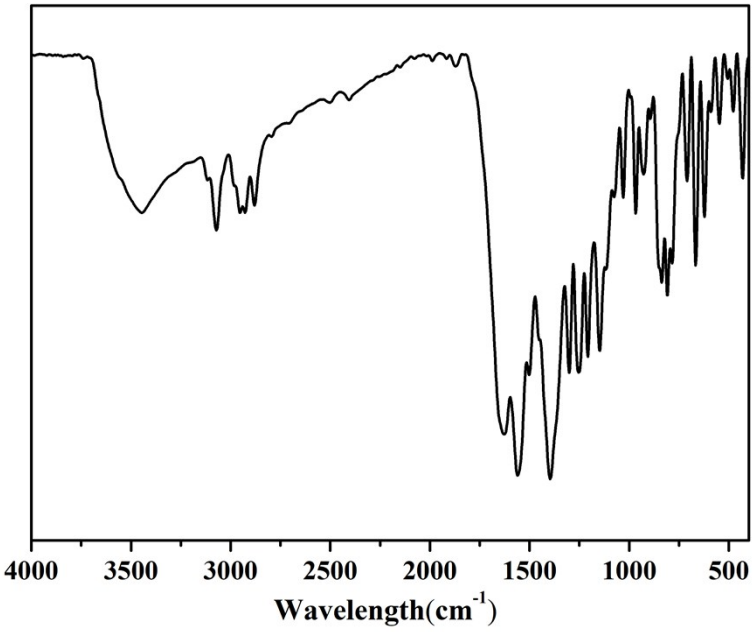
Wavelength(cm-1)

(a)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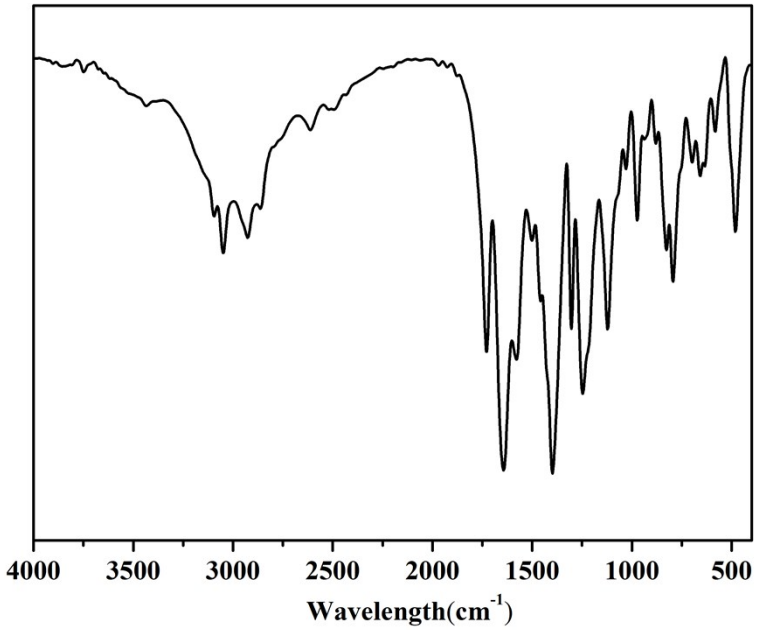
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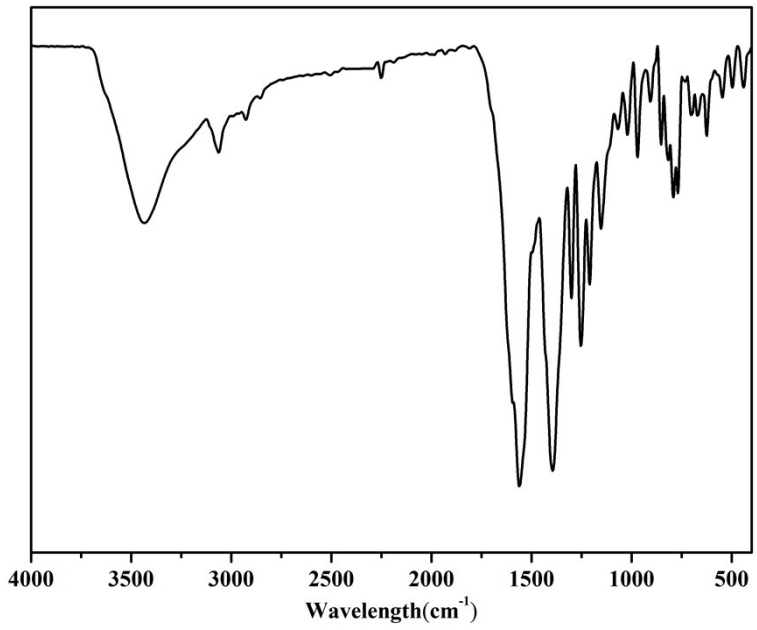
(c)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(d)

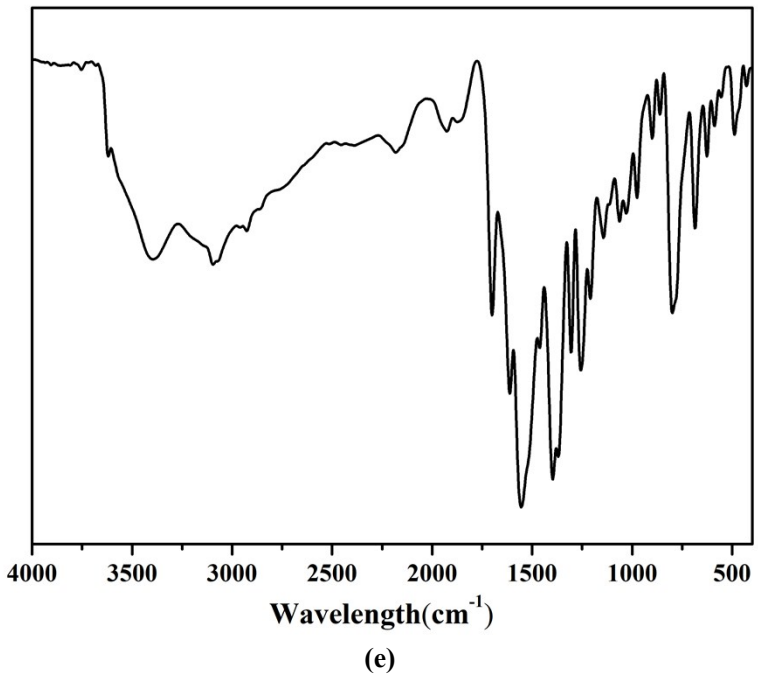


Fig. S1 The IR spectra for complexes **1(a)**, **2(b)**, **3(c)**, **4(d)** and **5(e)**.

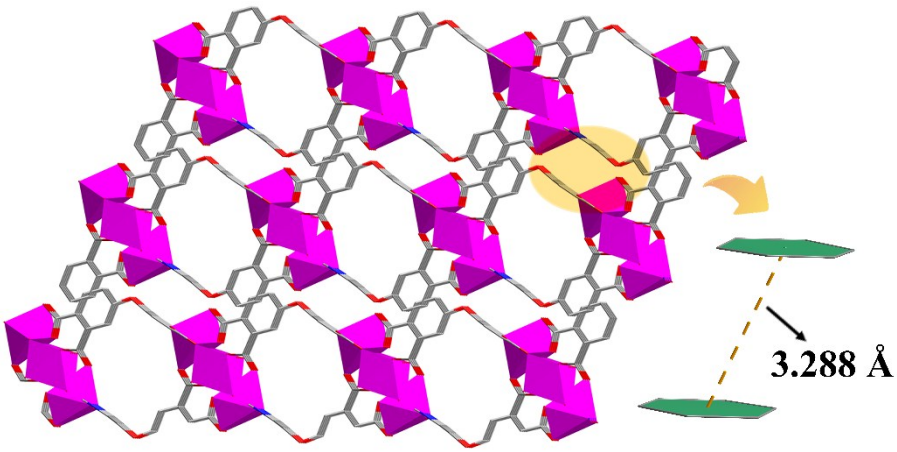
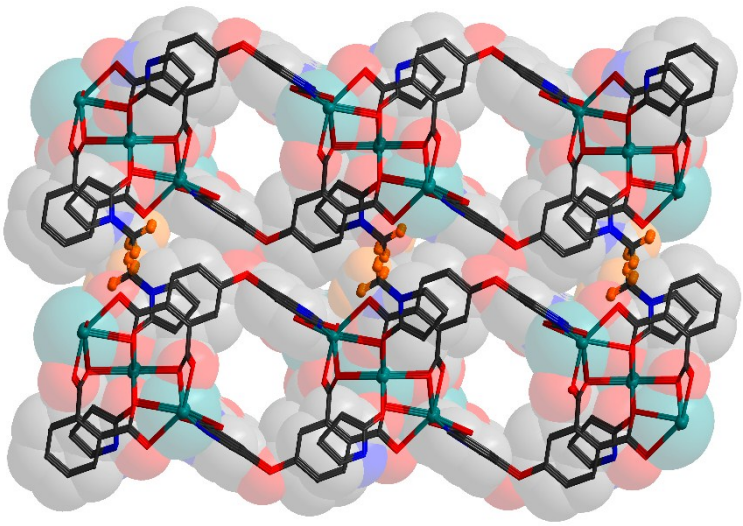


Fig. S2 Intermolecular π···π interactions between the phenyl rings of L^{3-} in **1**.



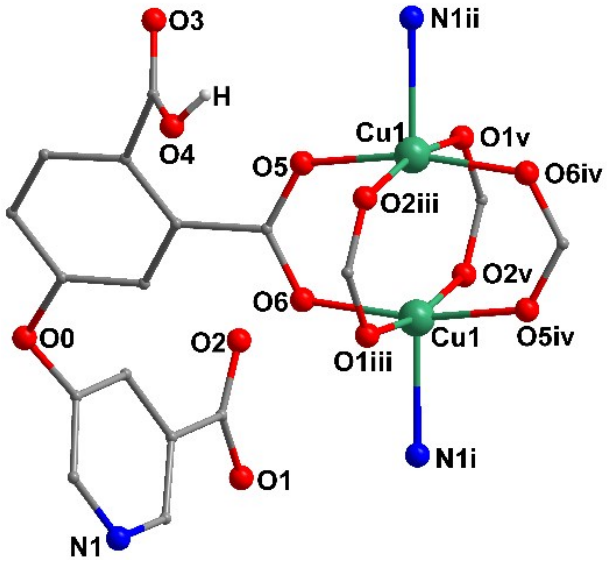
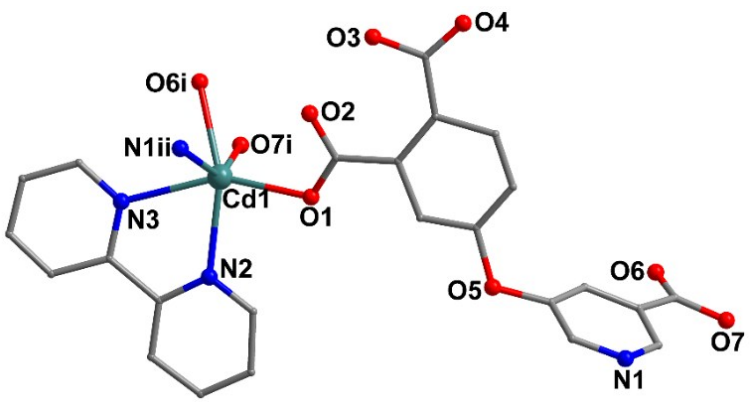
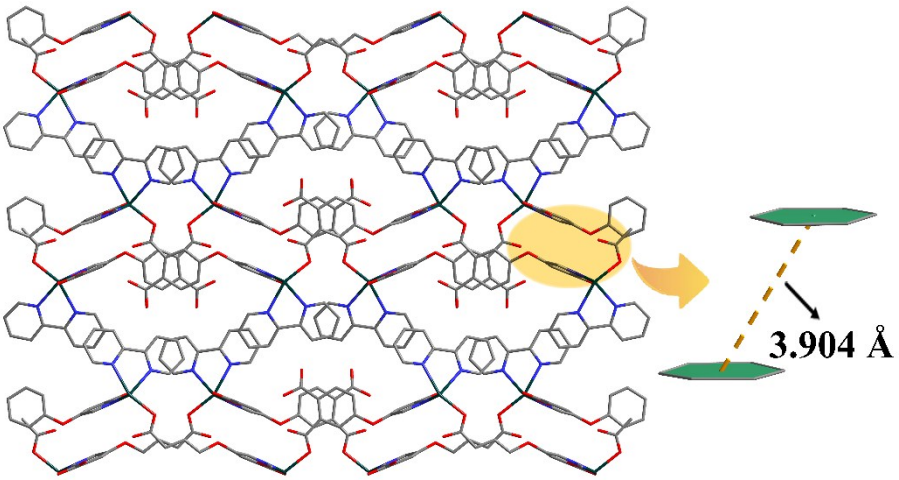


Fig. S3 3D supramolecular network of **2**.

Fig. S4 Coordination environments of Cu(II) ions in **3**. (Symmetry codes: i 1-x, 0.5+y, 0.5-z; ii x, 1.5-y, -0.5+z; iii x, 1+y, z; iv 1-x, 2-y, -z; v 1-x, 1-y, -z.)

Fig. S5 Coordination environments of Cd(II) ions in **4**. (Symmetry codes: i 0.5+x, 1.5-y, -z; ii 0.5+x, 0.5-y, -z.)





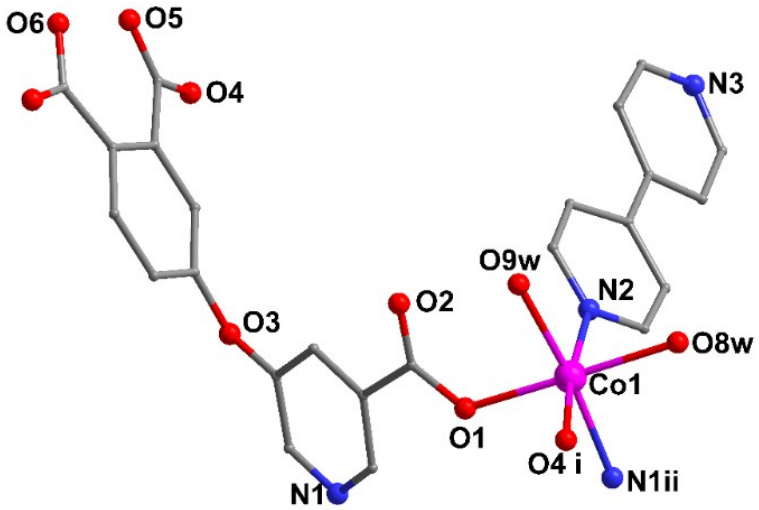
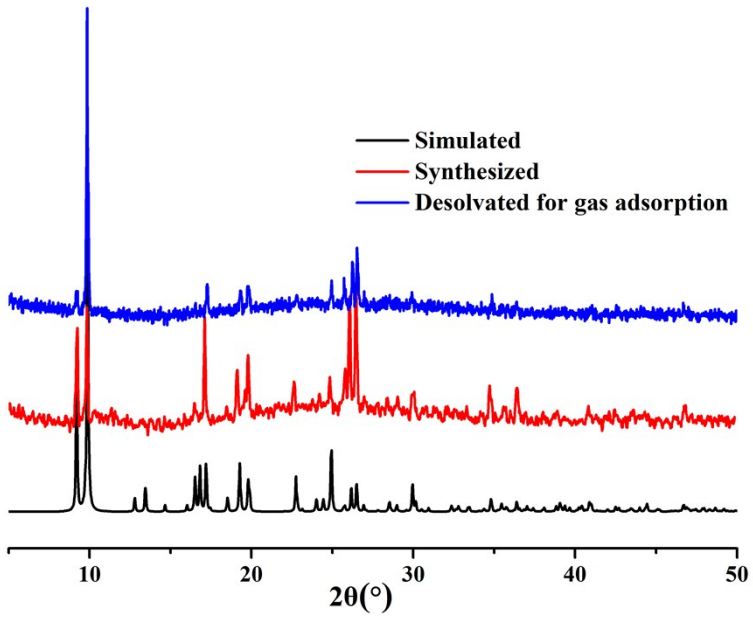


Fig. S6 Intermolecular π···π interactions between the phenyl rings of L^{3-} in **4**.

Fig. S7 Coordination environments of Co(II) ions in **5**. (Symmetry codes: i 1+x, 1+ y, z; ii 1-x, 1-y, 2-z.)


Simulated
Synthesized
Desolvated for gas adsorption
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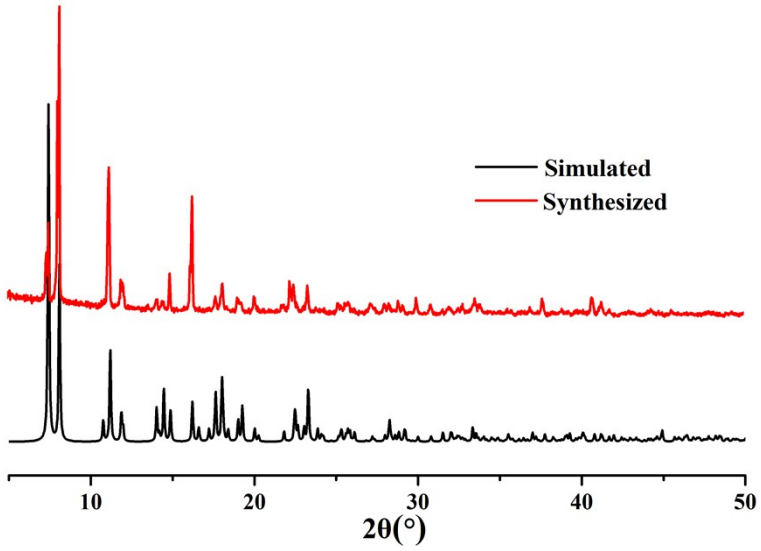
30
40
50
2θ(°)

(a)


Simulated
Synthesized
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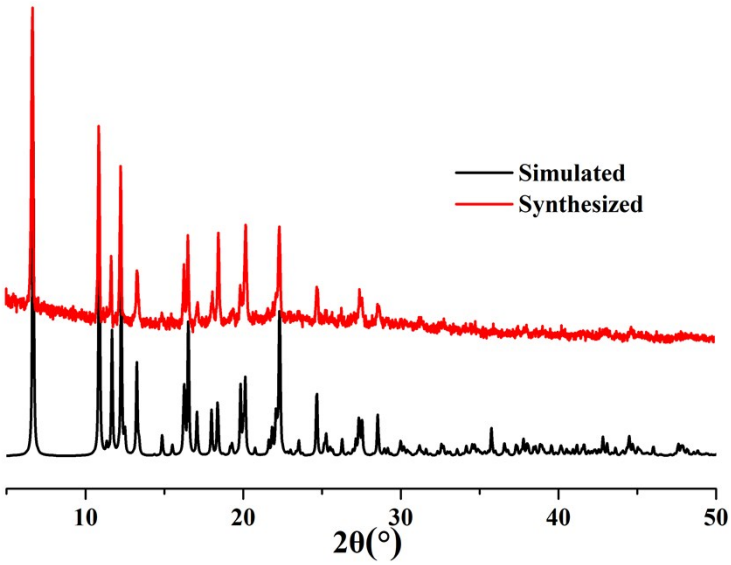
30
40
50
2θ(°)

(b)


Simulated
Synthesized
10
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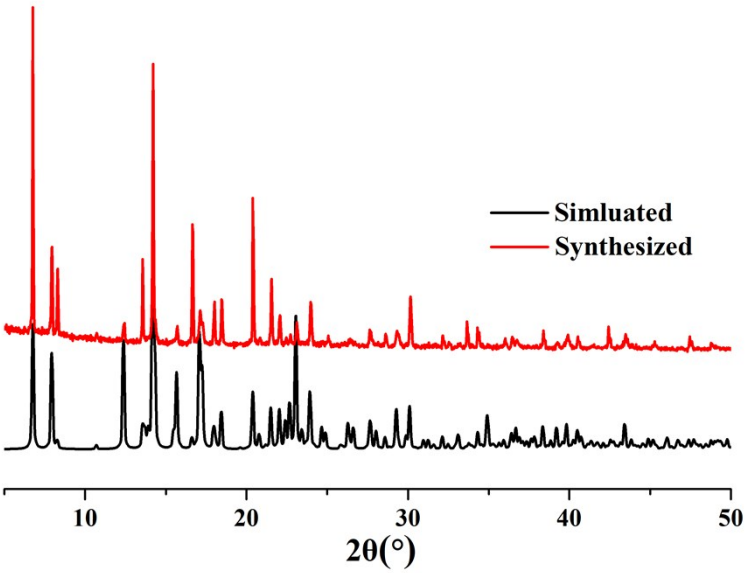
30
40
50
2θ(°)

(c)


Simluated
Synthesized
10
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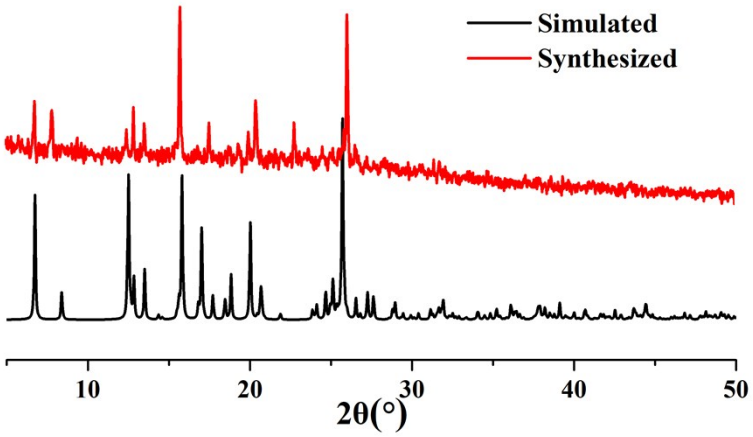
2θ(°)

(d)



(e)

Fig. **S8** PXRD patterns of complexes **1(a)**, **2(b)**, **3(c)**, **4(d)** and **5(e)** simulated from the X-ray single-crystal structure, experimental samples and desolvated samples.

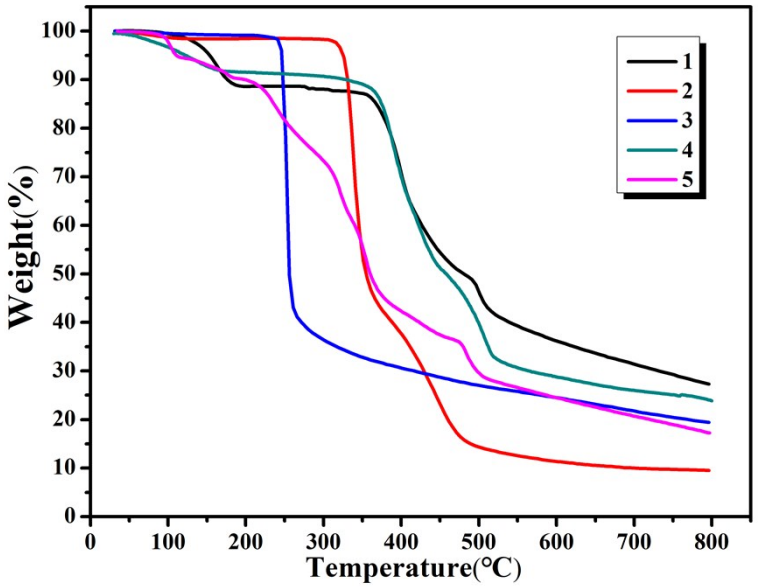


Fig. S9 TGA curves of **1-5**.

CO_2/CH_4 selectivity predication via IAST

The experimental isotherm data for pure CO_2 and CH_4 were fitted using a dual Langmuir-Freundlich (L-F) model:

$$q = \frac{a * b * p^c}{1 + b * p^c}$$

Where q and p are adsorbed amounts and pressures of component I, respectively. The adsorption selectivity for binary mixtures of CO_2/CH_4 at 273 and 298 K, defined by

$S_{ads} = (q1/q2)/(p1/p2)$

Where *qi* is the amount of *i* adsorbed and *pi* is the partial pressure of *i* in the mixture.

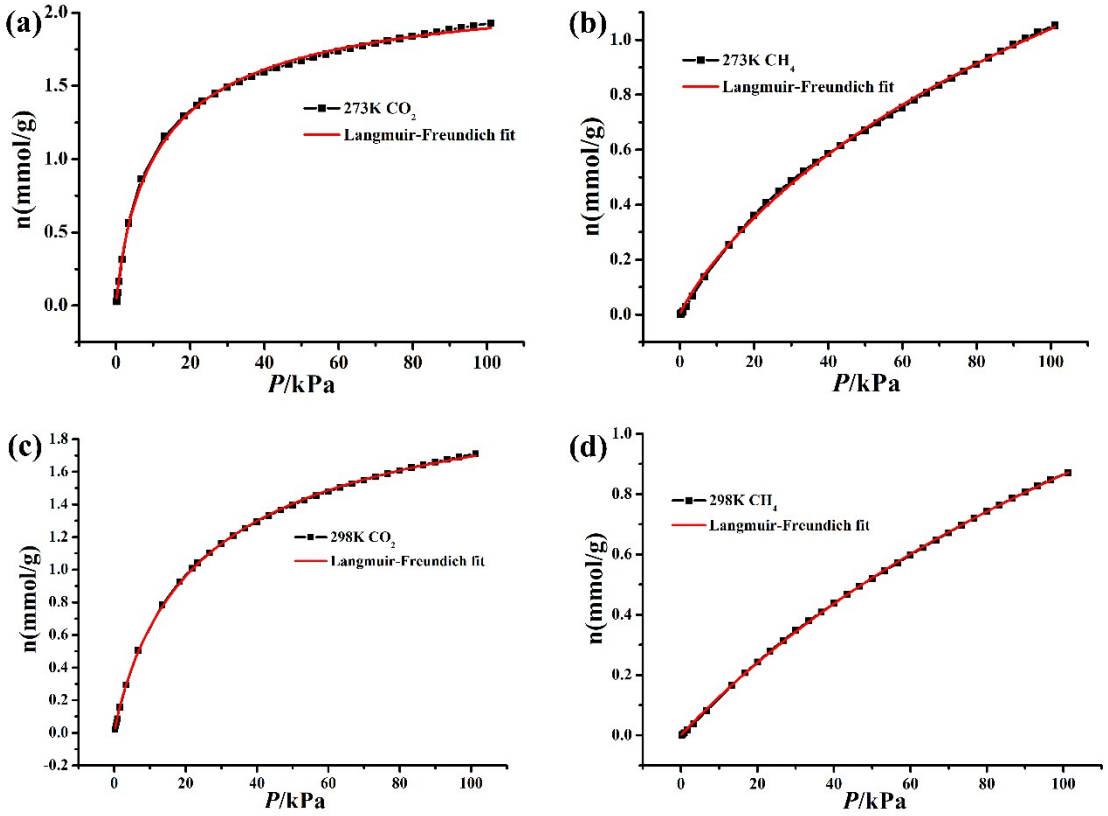
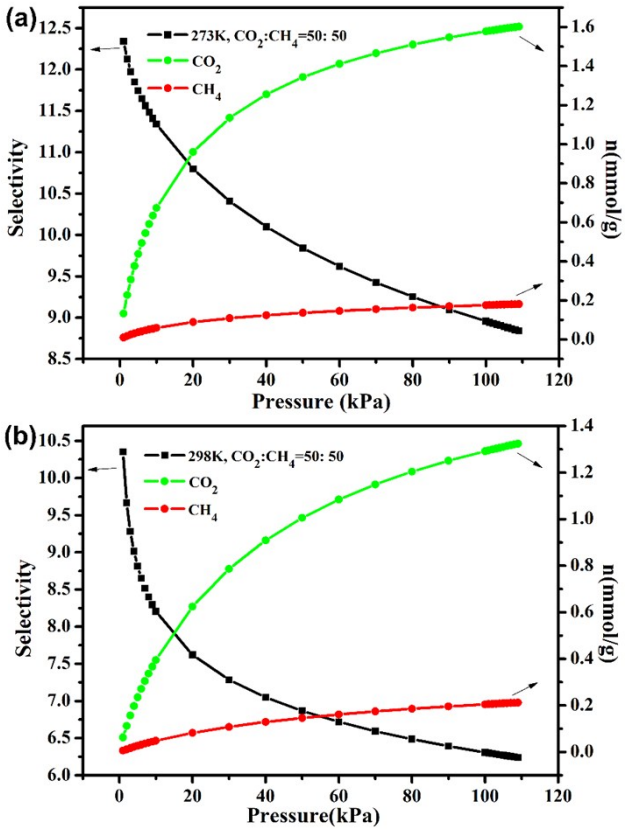


Fig. S10 (a) CO_2 adsorption isotherms of complex **1** with fitted- by dual L-F model :273 K, a = 2.2208, b = 0.1165, c = 0.8474, Chi^2 = 4.39 × 10^{-5}, R^2 = 0.99881; (b) CH_4 adsorption isotherms



of complex **1** with fitted- by dual L-F model :273 K, a = 2.9928, b = 0.0101, c = 0.86, Chi^2 = 8。18 × 10^{-5}, R^2 = 0.99927; (C) CO_2 adsorption isotherms of complex **1** with fitted- by dual L-F model :298 K, a = 2.237, b = 0.053, c = 0.883 , Chi^2 = 6.30 × 10^{-5}, R^2 = 0.9998; (d) CH_4 adsorption isotherms of complex **1** with fitted- by dual L-F model :298 K, a = 2.6642, b = 0.0053, c = 0.9788, Chi^2 = 1.07 × 10^{-5}, R^2 = 0.99987.

Fig. S11 IAST adsorption selectivity of 1 for equimolar mixtures of CO_2/CH_4 at 273 and 298 K.

Calculation of adsorption heat for CO_2 uptake using Viral 2 model

$$ln = \ln N + 1/T\sum_{i=0}^{m} aiN^I + \sum_{i=0}^{n} biN^i$$

$$Q_{st} = -R\sum_{i=0}^{m} aiN^i$$

The above equation was applied to fit the combined CO_2 isotherm data for desolvated **1** at 273K and 298K, where *P* is pressure, N is the adsorbed amount, T is the temperature, *ai* and *bi* are virial coefficients, and *m* and *n* are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and *R* is the universal gas constant.

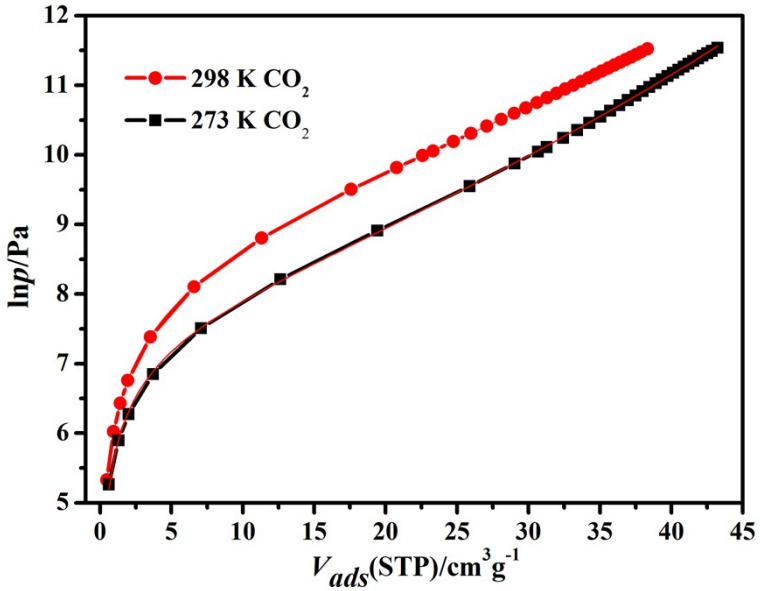


Fig. S12 Virial analysis of CO_2 adsorption data at 273 and 298K for **1**. Fitting results: a0 = -1816.47, a1 = -151.84, a2 = 6.205, a3 = -0.6557, a4 = 9.97×10^{-5}, Chi^2 = 2.3018×10^{-5}, R^2 = 0.99992.

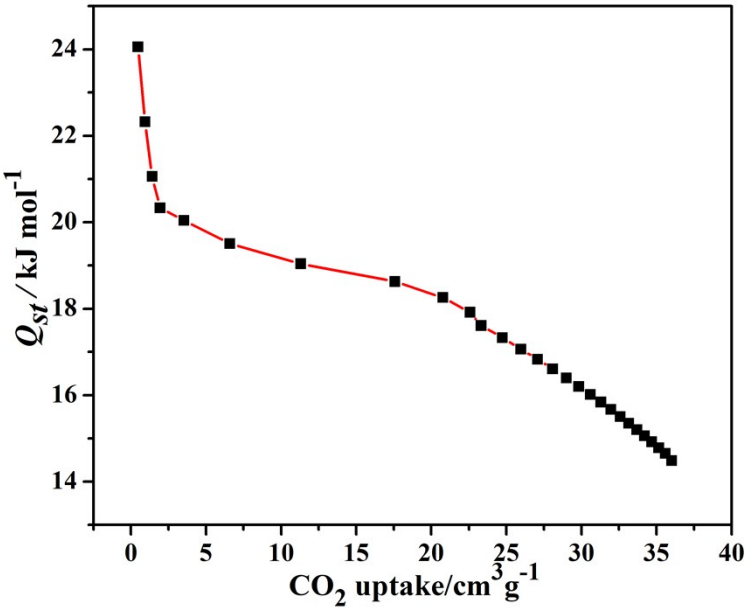


Fig. S13 Isosteric heat of CO_2 adsorption for **1** estimated by the virial equation from the adsorption isotherms at 273 and 298K.

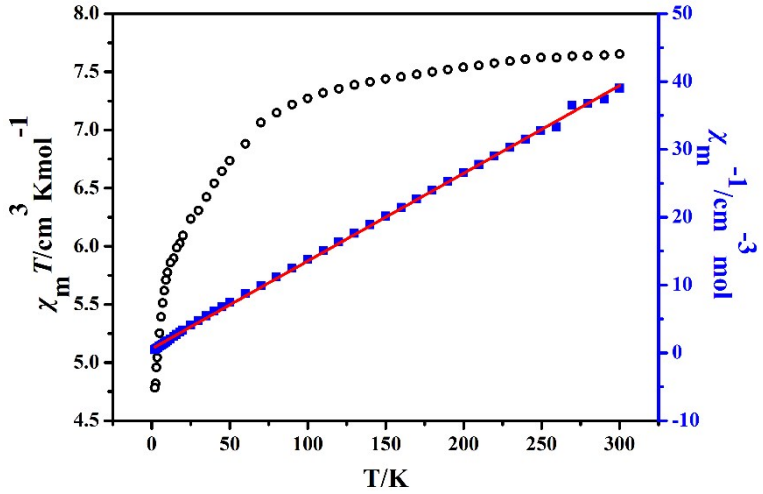


Fig. S14 The $\chi_m T$ and χ_m^{-1} (inset) versus T plots for **1**.

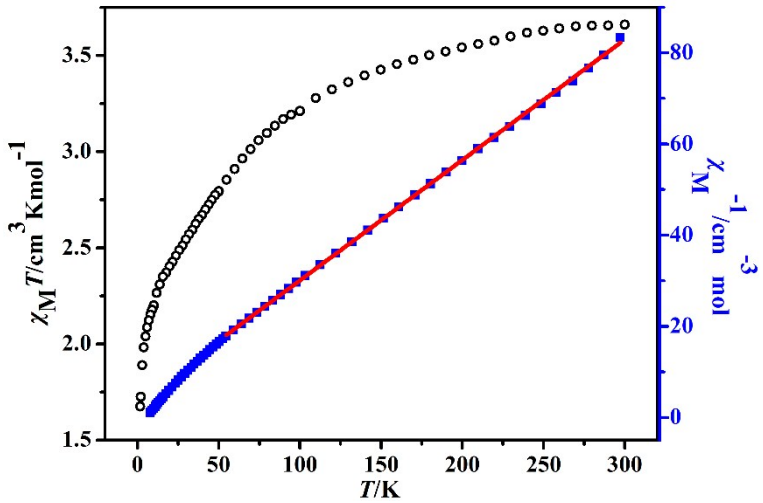


Fig. S15 The $\chi_m T$ and χ_m^{-1} (inset) versus T plots for **5**.

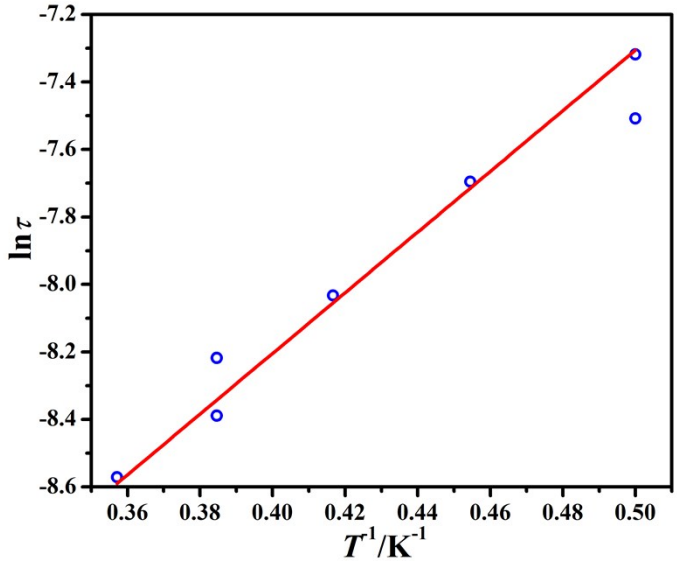


Fig. S16 lnτ versus T^{-1} plot for **2** under 1500Oe dc field from the Core-Core data (U_{eff} = 8.98 K; τ_0 = 7.58 × 10^{-6} s) the sold red lines are Arrhenius laws discussed in the paper.

Table. S1 Crystal data and structure refinement for **1-5**.

Complexes	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{28}H_{22}Co_3N_2O_{20}$	$C_{38}H_{30}Cd_3N_4O_{16}$	$C_{19}H_{16}CuN_2O_8$	$C_{24}H_{15}CdN_3O_7$	$C_{24}H_{18}CoN_3O_9$
Formula mass	885.23	1135.86	463.88	569.80	551.34
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	*P-1*	*C2/c*	*$P2_1/c$*	*Pbca*	*P-1*
a [Å]	7.838(2)	31.709(9)	13.390(8)	21.331(5)	7.5476(13)
b [Å]	10.632(3)	7.843(2)	9.643(6)	7.9294(19)	11.701(2)
c [Å]	10.783(3)	21.873(6)	15.340(10)	26.114(6)	14.477(3)
α [°]	114.411(4)	90	90	90	109.368(3)
β [°]	94.739(5)	131.327(4)	99.263(12)	90	100.819(3)
γ [°]	104.111(5)	90	90	90	102.451(3)
V [Å^3]	776.3(4)	4085.1(19)	1955.0(2)	4417.0(18)	1130.2(4)
Z	1	4	4	8	2
$D_{calcd.}$[mg·cm^{-3}]	1.778	1.847	1.576	1.714	1.620
μ [mm^{-1}]	1.669	1.625	1.168	1.042	0.823
F [000]	417	2232	948	2272	564
Reflections	4053 / 2868	10020 / 3820	11802 / 4686	20840 / 3887	5934 / 4176
R_{int}	0.0266	0.0401	0.1072	0.1338	0.0242
θ [°]	2.120-25.677	2.579-25.679	1.541-28.227	1.560-25.027	1.554-25.679
Goodness-of-fit on F^2	1.129	1.051	0.973	0.985	1.166
Final $R^{[a,b]}$ indices	R1 = 0.0637	R_1 = 0.0318	R_1 = 0.0681	R_1 = 0.0495	0.0690
[$I>2\sigma(I)$]	wR2 = 0.1998	wR_2 = 0.0790	wR_2 = 0.1546	wR_2 = 0.0860	0.1950

[a]$R_1=\sum||F_o|-|F_c||/\sum|F_o|$, [b]$wR_2=[\sum w(F_o^2- F_c^2)^2/ \sum w(F_o^2)^2]^{1/2}$

Table. S2 Selected bond lengths (Å) and bong angles (°) for **1-5**.

Complex **1**			
Co(1)-O(2)#1	2.055(4)	O(2)-Co(1)-O(8)	89.65(18)
Co(1)-O(2)	2.055(4)	O(2)#1-Co(1)-O(8)#1	89.65(18)
Co(1)-O(7)#2	2.118(4)	O(7)#3-Co(1)-O(7)#2	180.0
Co(1)-O(7)#3	2.118(4)	O(8)#1-Co(1)-O(7)#2	91.97(18)
Co(1)-O(8)	2.084(5)	O(8)#1-Co(1)-O(7)#3	88.03(18)
Co(1)-O(8)#1	2.084(5)	O(8)-Co(1)-O(7)#2	88.03(18)
Co(2)-N(1)	2.073(5)	O(8)-Co(1)-O(7)#3	91.97(18)
Co(2)-O(1)#4	2.008(4)	O(8)-Co(1)-O(8)#1	180.0
Co(2)-O(7)#5	2.387(4)	N(1)-Co(2)-O(7)#5	157.64(17)
Co(2)-O(6)#5	2.025(4)	O(1)#4-Co(2)-N(1)	96.31(18)
Co(2)-O(3)#6	2.002(4)	O(1)#4-Co(2)-O(7)#5	90.44(17)
O(2)#1-Co(1)-O(2)	180.00(17)	O(1)#4-Co(2)-O(6)#5	105.1(2)
O(2)-Co(1)-O(7)#2	88.28(17)	O(6)#5-Co(2)-N(1)	98.99(18)
O(2)#1-Co(1)-O(7)#3	88.28(17)	O(6)#5-Co(2)-O(7)#5	58.65(15)
O(2)-Co(1)-O(7)#3	91.72(17)	O(3)#6-Co(2)-N(1)	102.76(19)
O(2)#1-Co(1)-O(7)#2	91.72(17)	O(3)#6-Co(2)-O(1)#4	103.54(18)
O(2)#1-Co(1)-O(8)	90.35(18)	O(3)#6-Co(2)-O(7)#5	96.29(16)

O(2)-Co(1)-O(8)#1	90.35(18)	O(3)#6-Co(2)-O(6)#5	141.54(19)

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

Complex **2**

Cd(1)-O(1)	2.48(2)	O(7A)#1-Cd(1)-N(1)#3	109.0(2)
Cd(1)-O(2)	2.291(9)	O(7A)#1-Cd(1)-O(4A)#1	52.6(2)
Cd(1)-O(4)#1	2.390(5)	O(7A)#1-Cd(1)-O(6A)#2	98.8(3)
Cd(1)-O(5)#2	2.283(6)	O(7A)#1-Cd(1)-O(5A)#2	151.8(3)
Cd(1)-N(1)#3	2.321(3)	O(7A)#1-Cd(1)-O(1A)	105.9(15)
Cd(1)-O(7)#1	2.410(7)	O(6A)#2-Cd(1)-O(4A)#1	71.0(2)
Cd(1)-O(4A)#1	2.585(6)	O(6A)#2-Cd(1)-O(5A)#2	53.0(2)
Cd(1)-O(7A)#1	2.319(8)	O(5A)#2-Cd(1)-O(4A)#1	109.9(2)
Cd(1)-O(6A)#2	2.406(6)	O(2A)-Cd(1)-N(1)#3	139.7(5)
Cd(1)-O(5A)#2	2.419(7)	O(2A)-Cd(1)-O(4A)#1	134.7(7)
Cd(1)-O(2A)	2.31(2)	O(2A)-Cd(1)-O(7A)#1	89.9(11)
Cd(1)-O(1A)	2.34(4)	O(2A)-Cd(1)-O(6A)#2	94.8(8)
Cd(2)-O(4)#4	2.359(5)	O(2A)-Cd(1)-O(5A)#2	91.9(12)
Cd(2)-O(4)	2.359(5)	O(2A)-Cd(1)-O(1A)	56.1(13)
Cd(2)-O(6)	2.238(5)	O(1A)-Cd(1)-O(4A)#1	147.8(13)
Cd(2)-O(6)#4	2.238(5)	O(1A)-Cd(1)-O(6A)#2	140.8(12)
Cd(2)-O(4A)#4	2.225(6)	O(1A)-Cd(1)-O(5A)#2	98.4(14)
Cd(2)-O(4A)	2.225(6)	O(4)#4-Cd(2)-O(4)	78.7(3)
Cd(2)-O(6A)#4	2.352(6)	O(6)-Cd(2)-O(4)	80.30(19)
Cd(2)-O(6A)	2.352(6)	O(6)#4-Cd(2)-O(4)#4	80.30(19)
Cd(2)-O(8)	2.184(6)	O(6)#4-Cd(2)-O(4)	78.9(2)
Cd(2)-O(8A)#4	2.231(6)	O(6)-Cd(2)-O(4)#4	78.9(2)
Cd(2)-O(8A)	2.231(6)	O(6)-Cd(2)-O(6)#4	153.0(3)
Cd(1)-O(1)	2.48(2)	O(4A)#4-Cd(2)-O(4A)	150.7(3)
Cd(1)-O(2)	2.291(9)	O(4A)#4-Cd(2)-O(6A)#4	78.9(2)
Cd(1)-O(4)#1	2.390(5)	O(4A)-Cd(2)-O(6A)	78.9(2)
Cd(1)-O(5)#2	2.283(6)	O(4A)-Cd(2)-O(6A)#4	78.7(2)
Cd(1)-N(1)#3	2.321(3)	O(4A)#4-Cd(2)-O(6A)	78.7(2)
O(4)#1-Cd(1)-O(7)#1	54.0(2)	O(4A)-Cd(2)-O(8A)	98.8(2)
O(5)#2-Cd(1)-O(1)	94.5(6)	O(4A)#4-Cd(2)-O(8A)	97.9(2)
O(5)#2-Cd(1)-O(2)	90.1(10)	O(4A)#4-Cd(2)-O(8A)#4	98.8(2)
O(5)#2-Cd(1)-O(4)#1	93.6(2)	O(4A)-Cd(2)-O(8A)#4	97.9(2)
O(5)#2-Cd(1)-N(1)#3	114.7(2)	O(6A)#4-Cd(2)-O(6A)	79.5(3)
O(5)#2-Cd(1)-O(7)#1	147.2(2)	O(8)-Cd(2)-O(4)#4	163.3(2)
N(1)#3-Cd(1)-O(1)	85.2(5)	O(8)-Cd(2)-O(4)	84.7(2)
N(1)#3-Cd(1)-O(4)#1	115.90(16)	O(8)-Cd(2)-O(6)	96.9(2)
N(1)#3-Cd(1)-O(7)#1	87.3(2)	O(8)-Cd(2)-O(6)#4	98.2(2)
N(1)#3-Cd(1)-O(4A)#1	82.31(15)	O(8A)#4-Cd(2)-O(6A)	164.8(2)
N(1)#3-Cd(1)-O(6A)#2	115.99(17)	O(8A)#4-Cd(2)-O(6A)#4	85.3(2)

N(1)#3-Cd(1)-O(5A)#2	87.3(2)	O(8A)-Cd(2)-O(6A)	85.3(2)
N(1)#3-Cd(1)-O(1A)	84.1(12)	O(8A)-Cd(2)-O(6A)#4	164.8(2)
O(7)#1-Cd(1)-O(1)	112.1(6)	O(8A)#4-Cd(2)-O(8A)	110.0(4)
O(7A)#1-Cd(1)-O(6A)#2	98.8(3)	O(7A)#1-Cd(1)-N(1)#3	109.0(2)
O(7A)#1-Cd(1)-O(5A)#2	151.8(3)	O(7A)#1-Cd(1)-O(4A)#1	52.6(2)
O(7A)#1-Cd(1)-O(1A)	105.9(15)		

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

Complex **3**

Cu(1)-O(1)	1.981(4)	O(5) #3-Cu(1)-O(6)#4	166.46(17)
Cu(1)-O5#2	1.961(4)	O(5) #3-Cu(1)-N(0AA)#2	95.35(18)
Cu(1)- O(2) #1	1.965(4)	O(2) #1-Cu(1)-O(1)	167.36(17)
Cu(1)-O(6)#3	1.966(4)	O(2) #1-Cu(1)-O(6)#4	91.38(18)
Cu(1)-N(0AA) #4	2.202(5)	O(2) #1-Cu(1)-N(0AA)#2	106.57(18)
O(1)-Cu(1)-N(0AA)#2	86.07(18)	O(6) #4-Cu(1)-O(1)	87.30(19)
O(5) #3-Cu(1)-O(1)	89.08(19)	O(6) #4-Cu(1)-N(0AA)#2	97.41(17)
O(5) #3-Cu(1)-O(2)#1	89.30(18)		

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

Complex **4**

Cd(1)-O(1)	2.250(4)	O(6)#1-Cd(1)-N(2)	87.72(17)
Cd(1)-O(6)#1	2.397(4)	O(7)#1-Cd(1)-O(6)#1	55.29(16)
Cd(1)-O(7)#1	2.326(4)	O(7)#1-Cd(1)-N(2)	93.97(17)
Cd(1)-N(1)#2	2.290(5)	O(7)#1-Cd(1)-N(3)	104.15(18)
Cd(1)-N(2)	2.406(5)	N(1)#2-Cd(1)-O(6)#1	87.75(18)
Cd(1)-N(3)	2.346(5)	N(1)#2-Cd(1)-O(7)#1	143.03(18)
O(1)-Cd(1)-O(6)#1	118.00(17)	N(1)#2-Cd(1)-N(2)	83.07(18)
O(1)-Cd(1)-O(7)#1	96.99(19)	N(1)#2-Cd(1)-N(3)	108.88(19)
O(1)-Cd(1)-N(1)#2	101.65(19)	N(3)-Cd(1)-O(6)#1	148.53(18)
O(1)-Cd(1)-N(2)	153.81(19)	N(3)-Cd(1)-N(2)	68.8(2)
O(1)-Cd(1)-N(3)	85.5(2)		

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

Complex **5**

Co(1)-O(1)	2.096(3)	O(4)#1-Co(1)-O(8)	85.63(15)
Co(1)-O(4)#1	2.130(4)	O(4)#1-Co(1)-O(9)	91.11(14)
Co(1)-O(8)	2.134(4)	O(4)#1-Co(1)-N(1)#2	85.45(15)
Co(1)-O(9)	2.136(4)	O(4)#1-Co(1)-N(2)	173.11(15)
Co(1)-N(1)#2	2.165(4)	O(8)-Co(1)-O(9)	91.62(16)
Co(1)-N(2)	2.189(4)	O(8)-Co(1)-N(1)#2	93.43(16)
O(1)-Co(1)-O(4)#1	95.83(15)	O(8)-Co(1)-N(2)	87.58(15)

O(1)-Co(1)-O(8)	178.50(13)	O(9)-Co(1)-N(1)#2	173.66(15)
O(1)-Co(1)-O(9)	88.02(15)	O(9)-Co(1)-N(2)	90.25(14)
O(1)-Co(1)-N(1)#2	87.04(15)	N(1)#2-Co(1)-N(2)	93.80(15)
O(1)-Co(1)-N(2)	90.96(15)		

Symmetry transformations used to generate equivalent atoms: #1: x+1,y+1,z; #2: -x+1,-y+1,-z+2.