Electronic Supplementary Information

Two coordination polymers constructed from a multidentate carboxylic acid ligand with tertiary amine serve as acid-base catalysts for the synthesis of chloropropene carbonate from CO_2 under atmospheric pressure

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Fig. S1 The structural formula of ligand H_3pdcd

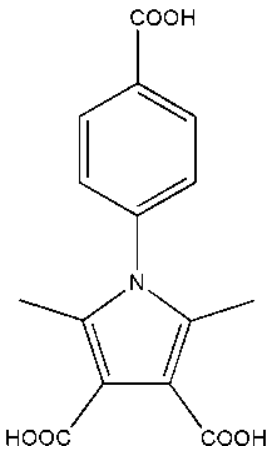

Fig. S2 Infrared spectra of fresh and recovered **1** were obtained from KBr pellets on a Nicolet Impact 5700 FTIR spectrometer in the 4000–400 cm^{-1} region. The strong absorption stretch at 1675 cm^{-1} indicated that the H_3pdcd ligands were partly deprotonated. The IR spectra of recovered **1** showed a new band at around 1796 cm^{-1}, which was ascribed to the adsorbed carbonyl group of cyclic carbonate.

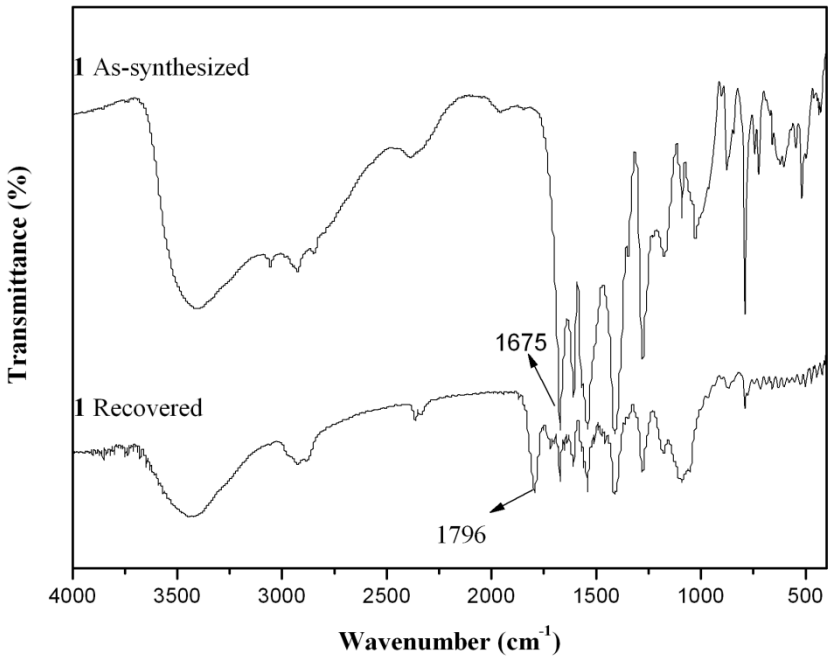

Fig. S3 PXRD patterns of simulated **2** from single-crystal X-ray data and as-synthesized **2**.

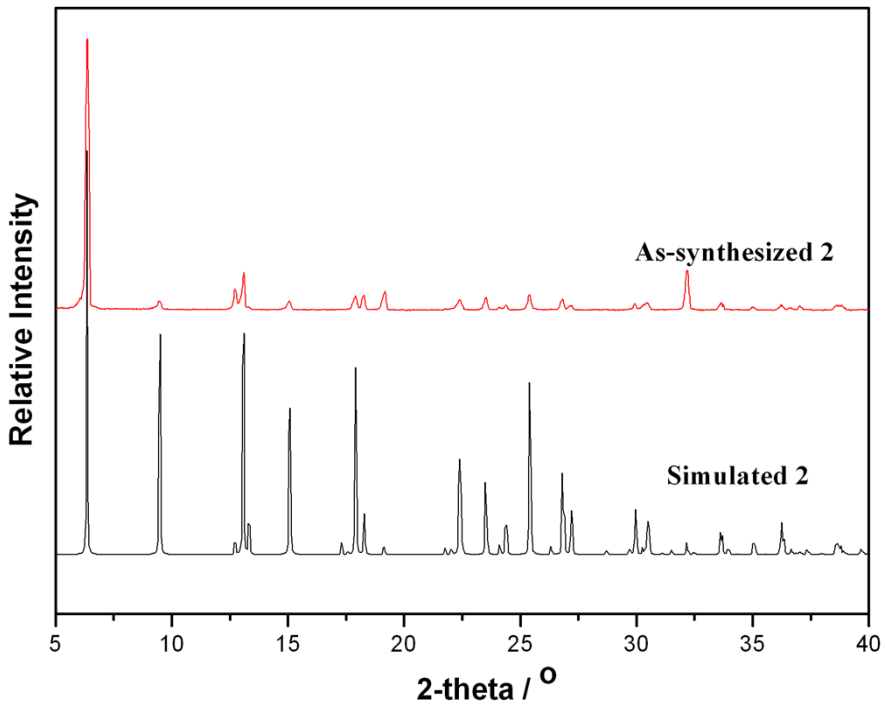

Fig. S4 TGA curves for **1** (–) and **2** (---).

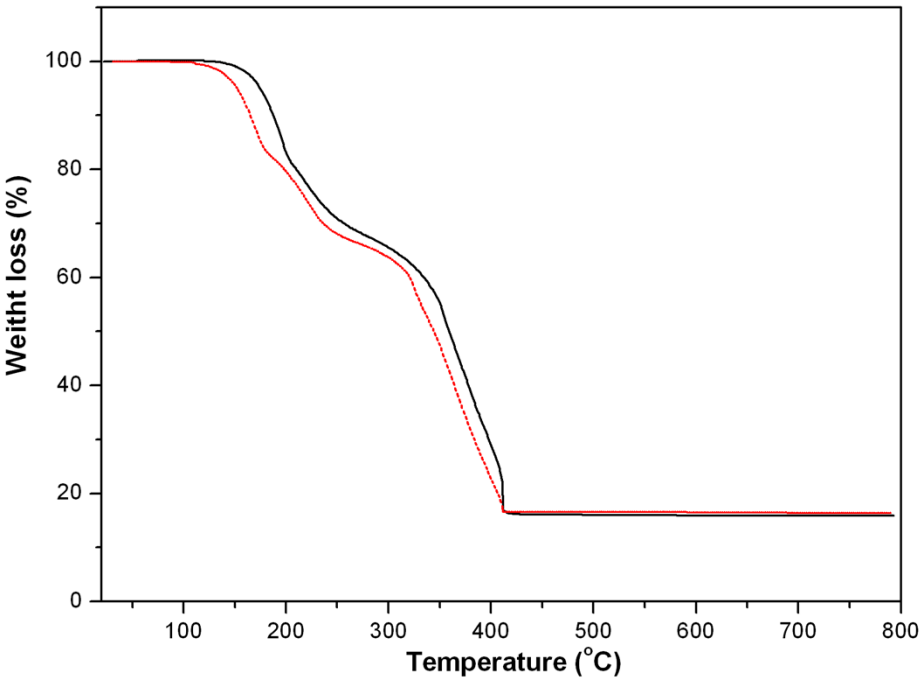

Fig. S5 FT-IR spectroscopy of adsorbed pyridine for compound 1.

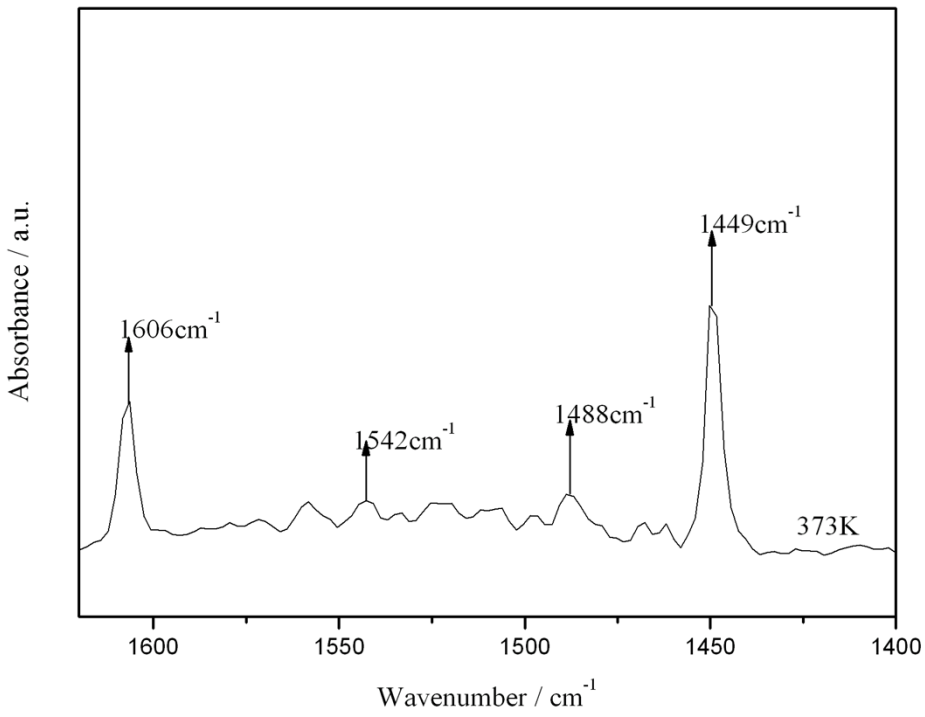

Fig. S6 Chloropropene carbonate yield versus reaction time (a) and temperature (b) for **1**.

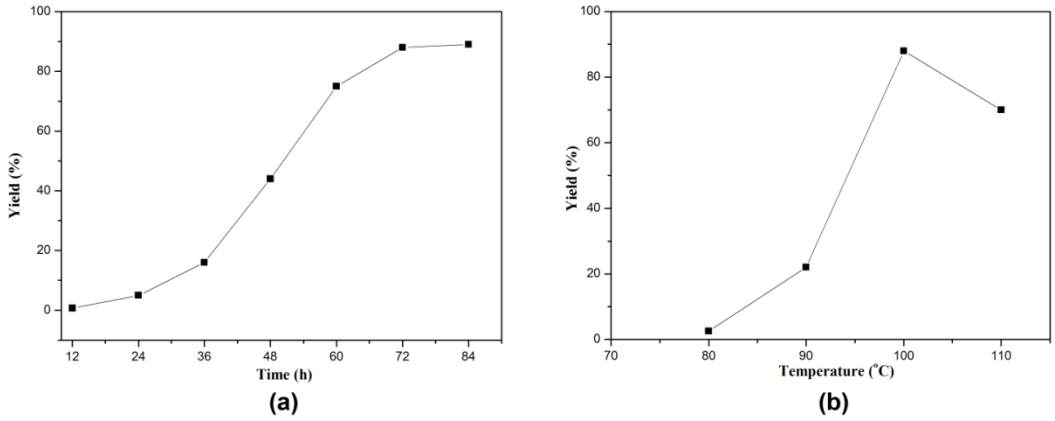

Fig. S7 HRTEM images of the fresh (a) and recovered (b) samples of **1**

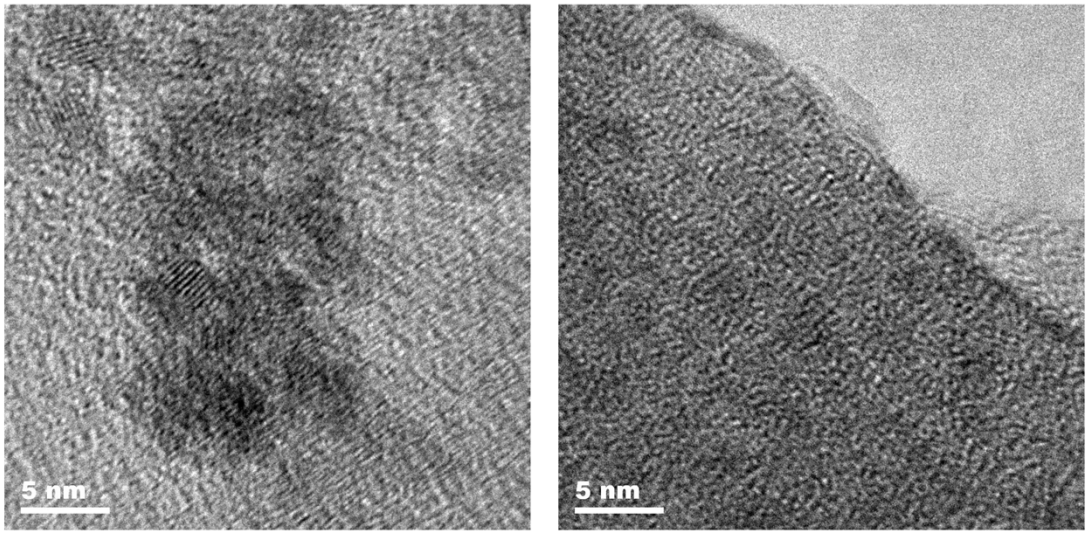

Table S1. Crystal Data and Structure Refinement for 1 and 2

Compounds	**1**	**2**
Empirical formula[a]	C18 H24 Ni N2 O10	C18 H24 Co N2 O10
Formula weight	487.10	487.32
Crystal system	Orthorhombic	Orthorhombic
Space group	Cmcm	Cmcm
Unit cell dimensions (Å and °)	a = 9.9158(2) Å b = 27.7237(5) Å c = 7.45820(10) Å	a = 9.9021(7) Å b = 27.824(2) Å c = 7.5624(6) Å
Volume (Å^3)	2050.28(6) Å^3	2083.6(3) Å^3
Z	4	4
Density (calculated) (Mg/m^3)	1.578	1.554
Absorption coefficient (mm^{-1})	1.006	0.882
F (000)	1016	1012
Crystal size (mm)	0.4 x 0.2 x 0.05	0.3 x 0.2 x 0.05
θ range for data collection	1.47 to 27.49 °	2.93 to 27.76 °
Limiting indices	-12<=h<=12, -31<=k<=35, -9<=l<=9	-12<=h<=12, -36<=k<=36, -7<=l<=9
Reflections collected / unique	9454 / 1339 [R(int) = 0.0253]	9884 / 1384 [R(int) = 0.0463]
Completeness to theta = 27.49 for **1,** 27.76 and for **2**	99.8 %	99.2 %
Data / restraints / parameters	1339 / 35 / 141	1384 / 0 / 120
Goodness-of-fit on F^2	1.067	1.072
Final R indices [I>2σ(I)][b]	R_1= 0.0383, wR_2= 0.1200	R_1= 0.0510, wR_2= 0.1533
R indices (all data)	R_1= 0.0476, wR_2= 0.1422	R_1= 0.0617, wR_2= 0.1654
Largest diff. peak and hole	0.723 and -0.470 e.Å^{-3}	0.922 and -0.884

[a] Did not calculate the hydrogen atoms of guest DMF molecule due to its disorder.

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

Table S2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1

atom	x	y	z	U (eq)[a]
Ni(1)	5000	0	10000	20(1)
O(1)	4696(4)	652(1)	8950(4)	32(1)
O(2)	2076(3)	4003(1)	7500	51(1)
O(3)	3770(3)	4510(1)	7500	50(1)
O(4)	5000	-378(1)	7500	20(1)
O(5)	7053(4)	-92(2)	10275(11)	40(2)
N(1)	5000	2912(1)	7500	24(1)
C(1)	5000	2393(2)	7500	24(1)
C(2)	5000	2148(1)	9108(5)	36(1)
C(3)	5000	1649(1)	9101(5)	38(1)

C(4)	5000	1397(2)	7500	25(1)
C(5)	5000	851(2)	7500	26(1)
C(6)	3864(3)	3191(1)	7500	26(1)
C(7)	4271(3)	3666(1)	7500	24(1)
C(8)	2517(15)	2967(5)	7920(9)	27(1)
C(8')	2520(30)	2956(9)	7500	27(1)
C(9)	3292(4)	4069(1)	7500	32(1)
O(6)	5000	2965(4)	2660(50)	164(6)
N(2)	5000	3766(2)	2500	56(2)
C(10)	4319(16)	3363(6)	2500	81(4)
C(11)	6548(17)	3722(6)	2500	89(4)

[a]*U* (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 2

atom	x	y	z	*U* (eq)[a]
Co(1)	5000	0	10000	26(1)
O(1)	4709(5)	653(1)	8931(5)	38(2)
O(2)	2069(3)	3995(1)	7500	56(1)
O(3)	3774(3)	4502(1)	7500	48(1)
O(4)	5000	-391(1)	7500	25(1)
O(5)	7110(4)	0	10000	80(2)
N(1)	5000	2909(2)	7500	30(1)
C(1)	5000	2390(2)	7500	28(1)
C(2)	5000	2146(1)	9092(6)	41(1)
C(3)	5000	1649(1)	9084(6)	41(1)
C(4)	5000	1397(2)	7500	29(1)
C(5)	5000	853(2)	7500	30(1)
C(6)	3863(4)	3187(1)	7500	31(1)
C(7)	4275(4)	3660(1)	7500	28(1)
C(8)	2519(5)	2958(2)	7500	62(2)
C(9)	3289(4)	4061(1)	7500	37(1)
O(6)	5000	2950(4)	2131	130(4)
N(2)	5000	3750(3)	2500	63(2)
C(10)	4288(18)	3357(6)	2500	94(5)
C(11)	6550(20)	3727(7)	2500	101(5)
C(12)	4473(17)	4230(7)	2500	103(5)

[a]*U* (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S4 Selected bond lengths (Å) and angles (°) in 1.

Ni(1)-O(1)#1	1.992(3)	C(6)-C(8')	1.48(3)
Ni(1)-O(1)#2	1.992(3)	C(6)-C(8)#6	1.506(14)
Ni(1)-O(1)	1.992(3)	C(6)-C(8)	1.506(14)
Ni(1)-O(1)#3	1.992(3)	C(7)-C(7)#5	1.447(7)

Ni(1)-O(5)#1	2.063(4)	C(7)-C(9)	1.479(4)
Ni(1)-O(5)#2	2.063(4)	O(6)-C(10)#8	1.301(16)
Ni(1)-O(5)	2.063(4)	O(6)-C(10)	1.301(16)
Ni(1)-O(5)#3	2.063(4)	N(2)-C(10)	1.307(15)
Ni(1)-O(4)	2.1386(14)	N(2)-C(10)#8	1.307(15)
Ni(1)-O(4)#3	2.1386(14)	N(2)-C(12)#8	1.404(16)
O(1)-C(5)	1.252(4)	N(2)-C(12)	1.404(16)
O(2)-C(9)	1.218(5)	N(2)-C(11)#8	1.539(17)
O(3)-C(9)	1.312(4)	N(2)-C(11)	1.539(17)
O(4)-Ni(1)#4	2.1386(14)	C(4)-C(3)#6	1.383(4)
N(1)-C(6)#5	1.366(4)	C(4)-C(5)	1.514(6)
N(1)-C(6)	1.366(4)	C(5)-O(1)#6	1.252(4)
N(1)-C(1)	1.441(5)	C(5)-O(1)#5	1.252(3)
C(1)-C(2)#6	1.379(4)	C(5)-O(1)#1	1.252(3)
C(1)-C(2)	1.379(4)	C(6)-C(7)	1.380(4)
C(2)-C(3)	1.382(5)	C(3)-C(4)	1.383(4)
O(1)#1-Ni(1)-O(1)#2	180.00(7)	O(1)#6-C(5)-C(4)	116.2(2)
O(1)#2-Ni(1)-O(1)	162.6(2)	O(1)#5-C(5)-C(4)	116.2(2)
O(1)#1-Ni(1)-O(1)#3	162.6(2)	O(1)#1-C(5)-C(4)	116.2(2)
O(1)-Ni(1)-O(1)#3	180.00(7)	O(1)-C(5)-C(4)	116.2(2)
O(1)#1-Ni(1)-O(5)#1	107.51(17)	N(1)-C(6)-C(7)	107.4(3)
O(1)#2-Ni(1)-O(5)#1	72.49(17)	N(1)-C(6)-C(8')	119.5(10)
O(1)-Ni(1)-O(5)#1	90.09(17)	C(7)-C(6)-C(8')	133.1(11)
O(1)#3-Ni(1)-O(5)#1	89.91(17)	N(1)-C(6)-C(8)#6	119.9(6)
O(1)#1-Ni(1)-O(5)#2	72.49(17)	C(7)-C(6)-C(8)#6	130.8(6)
O(1)#2-Ni(1)-O(5)#2	107.51(17)	N(1)-C(6)-C(8)	119.9(6)
O(1)-Ni(1)-O(5)#2	89.91(17)	C(7)-C(6)-C(8)	130.8(6)
O(1)#3-Ni(1)-O(5)#2	90.09(17)	C(6)-C(7)-C(7)#5	107.0(2)
O(5)#1-Ni(1)-O(5)#2	180.0	C(6)-C(7)-C(9)	122.0(3)
O(1)#1-Ni(1)-O(5)	90.09(17)	C(7)#5-C(7)-C(9)	131.0(2)
O(1)#2-Ni(1)-O(5)	89.91(17)	O(2)-C(9)-O(3)	119.9(3)
O(1)-Ni(1)-O(5)	107.51(17)	O(2)-C(9)-C(7)	122.3(3)
O(1)#3-Ni(1)-O(5)	72.49(17)	O(3)-C(9)-C(7)	117.8(3)
O(5)#1-Ni(1)-O(5)	161.7(3)	O(6)#7-O(6)-C(10)#8	84.7(15)
O(1)#1-Ni(1)-O(5)#3	89.91(17)	O(6)#7-O(6)-C(10)	84.7(16)
O(1)#2-Ni(1)-O(5)#3	90.09(17)	C(10)-N(2)-C(12)#8	169.8(9)
O(1)-Ni(1)-O(5)#3	72.49(17)	C(10)#8-N(2)-C(12)#8	127.8(10)
O(1)#3-Ni(1)-O(5)#3	107.51(17)	C(10)-N(2)-C(12)	127.8(10)
O(5)#2-Ni(1)-O(5)#3	161.7(3)	C(10)#8-N(2)-C(12)	169.8(9)
O(5)-Ni(1)-O(5)#3	180.0	C(10)#8-N(2)-C(11)#8	116.6(11)
O(1)#1-Ni(1)-O(4)	95.81(11)	C(12)#8-N(2)-C(11)#8	115.5(10)
O(1)#2-Ni(1)-O(4)	84.19(11)	C(12)-N(2)-C(11)#8	73.5(9)
O(1)-Ni(1)-O(4)	95.81(11)	C(10)-N(2)-C(11)	116.6(11)

O(1)#3-Ni(1)-O(4)	84.19(11)	C(12)#8-N(2)-C(11)	73.5(9)
O(5)#1-Ni(1)-O(4)	91.5(3)	C(12)-N(2)-C(11)	115.5(10)
O(5)#2-Ni(1)-O(4)	88.5(3)	C(11)#8-N(2)-C(11)	170.9(14)
O(5)-Ni(1)-O(4)	91.5(3)	O(6)#7-C(10)-N(2)	117.3(12)
O(5)#3-Ni(1)-O(4)	88.5(3)	O(6)-C(10)-N(2)	117.3(12)
O(1)#1-Ni(1)-O(4)#3	84.19(11)	O(6)#7-C(10)-C(11)#8	169.3(15)
O(1)#2-Ni(1)-O(4)#3	95.81(11)	O(6)-C(10)-C(11)#8	169.3(15)
O(1)-Ni(1)-O(4)#3	84.19(11)	C(11)#8-C(10)-C(10)#8	130.8(10)
O(1)#3-Ni(1)-O(4)#3	95.81(11)	C(10)#8-C(11)-C(12)#8	103.4(14)
O(5)#1-Ni(1)-O(4)#3	88.5(3)	C(12)#8-C(12)-C(11)#8	125.9(8)
O(5)#2-Ni(1)-O(4)#3	91.5(3)	C(2)-C(1)-N(1)	119.5(2)
O(5)-Ni(1)-O(4)#3	88.5(3)	C(1)-C(2)-C(3)	119.3(3)
O(5)#3-Ni(1)-O(4)#3	91.5(3)	C(2)-C(3)-C(4)	120.5(3)
O(4)-Ni(1)-O(4)#3	180.0	C(3)-C(4)-C(3)#6	119.4(4)
O(1)#1-O(1)-C(5)	76.04(18)	C(3)-C(4)-C(5)	120.3(2)
O(1)#1-O(1)-Ni(1)	81.28(11)	C(3)#6-C(4)-C(5)	120.3(2)
C(5)-O(1)-Ni(1)	134.8(3)	O(1)#6-C(5)-O(1)#5	27.9(4)
Ni(1)-O(4)-Ni(1)#4	121.36(14)	O(1)#6-C(5)-O(1)#1	127.5(5)
O(5)#2-O(5)-Ni(1)	80.87(14)	O(1)#5-C(5)-O(1)#1	119.5(4)
C(6)#5-N(1)-C(6)	111.2(4)	O(1)#6-C(5)-O(1)	119.5(4)
C(6)#5-N(1)-C(1)	124.42(19)	O(1)#5-C(5)-O(1)	127.5(5)
C(6)-N(1)-C(1)	124.42(19)	C(2)#6-C(1)-N(1)	119.5(2)
C(2)#6-C(1)-C(2)	120.9(4)		

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

Table S5 Selected bond lengths (Å) and angles (°) in 2.

Co(1)-O(1)#1	2.009(3)	C(4)-C(5)	1.514(6)
Co(1)-O(1)	2.009(3)	C(5)-O(1)#6	1.250(4)
Co(1)-O(1)#2	2.009(3)	C(5)-O(1)#5	1.250(4)
Co(1)-O(1)#3	2.009(3)	C(5)-O(1)#1	1.250(4)
Co(1)-O(5)#3	2.089(4)	C(6)-C(7)	1.377(5)
Co(1)-O(5)	2.089(4)	C(6)-C(8)	1.476(5)
Co(1)-O(4)#3	2.1811(17)	C(7)-C(7)#5	1.435(8)
Co(1)-O(4)	2.1811(17)	C(7)-C(9)	1.483(5)
O(1)-C(5)	1.250(4)	O(6)-C(10)#8	1.364(17)
O(2)-C(9)	1.222(6)	O(6)-C(10)	1.364(17)
O(3)-C(9)	1.316(5)	N(2)-C(10)	1.301(18)
O(4)-Co(1)#4	2.1811(17)	N(2)-C(10)#8	1.301(18)
N(1)-C(6)#5	1.367(4)	N(2)-C(12)#8	1.435(18)
N(1)-C(6)	1.367(4)	N(2)-C(12)	1.435(18)
N(1)-C(1)	1.444(6)	N(2)-C(11)#8	1.54(2)
C(1)-C(2)	1.382(5)	N(2)-C(11)	1.54(2)
C(1)-C(2)#6	1.382(5)	C(10)-C(11)#8	1.32(2)

C(2)-C(3)	1.381(5)	C(10)-O(6)#7	1.364(17)
C(3)-C(4)	1.389(5)	C(10)-C(10)#8	1.41(4)
C(4)-C(3)#6	1.389(5)	C(11)-C(10)#8	1.32(2)
O(1)#1-Co(1)-O(1)#2	180.00(8)	O(1)#6-C(5)-O(1)#1	127.2(5)
O(1)-Co(1)-O(1)#2	163.5(3)	O(1)#5-C(5)-O(1)#1	119.9(5)
O(1)#1-Co(1)-O(1)#3	163.5(3)	O(1)-C(5)-C(4)	116.4(2)
O(1)-Co(1)-O(1)#3	180.00(8)	O(1)#6-C(5)-C(4)	116.4(2)
O(1)#1-Co(1)-O(5)#3	98.23(15)	O(1)#5-C(5)-C(4)	116.4(2)
O(1)-Co(1)-O(5)#3	81.77(15)	O(1)#1-C(5)-C(4)	116.4(2)
O(1)#2-Co(1)-O(5)#3	81.77(15)	N(1)-C(6)-C(7)	107.3(3)
O(1)#3-Co(1)-O(5)#3	98.23(15)	N(1)-C(6)-C(8)	119.9(3)
O(1)#1-Co(1)-O(5)	81.77(15)	C(7)-C(6)-C(8)	132.8(4)
O(1)-Co(1)-O(5)	98.23(15)	C(6)-C(7)-C(7)#5	107.3(2)
O(1)#2-Co(1)-O(5)	98.23(15)	C(6)-C(7)-C(9)	121.5(3)
O(1)#3-Co(1)-O(5)	81.77(15)	C(7)#5-C(7)-C(9)	131.2(2)
O(5)#3-Co(1)-O(5)	180.0	O(2)-C(9)-O(3)	120.1(4)
O(1)#1-Co(1)-O(4)#3	84.15(13)	O(2)-C(9)-C(7)	122.5(4)
O(1)-Co(1)-O(4)#3	84.15(13)	O(3)-C(9)-C(7)	117.4(4)
O(1)#2-Co(1)-O(4)#3	95.85(13)	O(6)#7-O(6)-C(10)#8	78.21(16)
O(1)#3-Co(1)-O(4)#3	95.85(13)	O(6)#7-O(6)-C(10)	78.21(15)
O(5)#3-Co(1)-O(4)#3	90.0	C(10)#8-O(6)-C(10)	62.3(16)
O(5)-Co(1)-O(4)#3	90.0	C(10)-N(2)-C(10)#8	65.7(16)
O(1)#1-Co(1)-O(4)	95.85(13)	C(10)-N(2)-C(12)#8	168.5(10)
O(1)-Co(1)-O(4)	95.85(13)	C(10)#8-N(2)-C(12)#8	125.8(11)
O(1)#2-Co(1)-O(4)	84.15(13)	C(10)-N(2)-C(12)	125.8(11)
O(1)#3-Co(1)-O(4)	84.15(13)	C(10)#8-N(2)-C(12)	168.5(10)
O(5)#3-Co(1)-O(4)	90.0	C(10)-N(2)-C(11)#8	54.8(10)
O(5)-Co(1)-O(4)	90.0	C(10)#8-N(2)-C(11)#8	120.5(12)
O(4)#3-Co(1)-O(4)	180.00(15)	C(12)#8-N(2)-C(11)#8	113.7(11)
O(1)#1-O(1)-C(5)	76.7(2)	C(12)-N(2)-C(11)#8	71.0(10)
O(1)#1-O(1)-Co(1)	81.77(15)	C(10)-N(2)-C(11)	120.5(12)
C(5)-O(1)-Co(1)	135.8(3)	C(10)#8-N(2)-C(11)	54.8(10)
Co(1)#4-O(4)-Co(1)	120.18(15)	C(12)#8-N(2)-C(11)	71.0(10)
C(6)#5-N(1)-C(6)	110.9(4)	C(12)-N(2)-C(11)	113.7(11)
C(6)#5-N(1)-C(1)	124.6(2)	C(11)#8-N(2)-C(11)	175.3(16)
C(6)-N(1)-C(1)	124.6(2)	N(2)-C(10)-C(11)#8	71.7(13)
C(2)-C(1)-C(2)#6	121.2(5)	N(2)-C(10)-O(6)	114.7(13)
C(2)-C(1)-N(1)	119.4(2)	C(11)#8-C(10)-O(6)	166.3(9)
C(2)#6-C(1)-N(1)	119.4(2)	N(2)-C(10)-O(6)#7	114.7(13)
C(3)-C(2)-C(1)	119.2(4)	C(11)#8-C(10)-O(6)#7	166.3(9)
C(2)-C(3)-C(4)	120.6(4)	N(2)-C(10)-C(10)#8	57.2(8)
C(3)#6-C(4)-C(3)	119.2(5)	C(11)#8-C(10)-C(10)#8	128.9(12)
C(3)#6-C(4)-C(5)	120.4(2)	O(6)-C(10)-C(10)#8	58.9(8)

C(3)-C(4)-C(5)	120.4(2)	O(6)#7-C(10)-C(10)#8	58.9(8)
O(1)-C(5)-O(1)#6	119.9(5)	C(10)#8-C(11)-N(2)	53.5(11)
O(1)-C(5)-O(1)#5	127.2(5)	C(10)#8-C(11)-C(12)#8	105.3(16)
C(12)#8-C(12)-C(11)#8	125.9(9)	N(2)-C(11)-C(12)#8	51.8(9)
N(2)-C(12)-C(11)#8	57.2(9)	C(12)#8-C(12)-N(2)	68.7(7)

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

Table S6. Hydrogen Bonds for 1 and 2

D–H···A	*d*(D–H)	*d*(H···A)	Angle	*d*(D···A)
Compound 1				
O(3)-H(3A)...O(3)#1	0.94(2)	1.52(3)	164(9)	2.439 (7)
O(4)-H(4)...O(2)#2	0.84(4)	1.84(4)	177(4)	2.681(4)
O(5)-H(5)...O(3)#2	0.93(2)	2.10(3)	145(4)	2.898 (9)
Compound 2				
O(3)-H(3A)...O(3)#5	0.95(2)	1.49(3)	168(9)	2.429(7)
O(4)-H(4)...O(2)#9	0.77(4)	1.89(4)	180(4)	2.669(4)
O(5)-H(5)...O(3)#9	0.924(19)	1.95(2)	171(5)	2.866(3)
O(5)-H(5)...O(2)#9	0.924(19)	2.69(4)	132(4)	3.377(3)

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