Electronic Supplementary Material (ESI) for CrystEngComm.

Construction and Structural Transformation of Two Coordination Sphere Supramolecular Isomers Based on Co(II) and 4-(2-Pyridyl)-NH-1,2,3-Triazole *via* One-Pot Synthesis

Supporting information

Supramolecular interactions

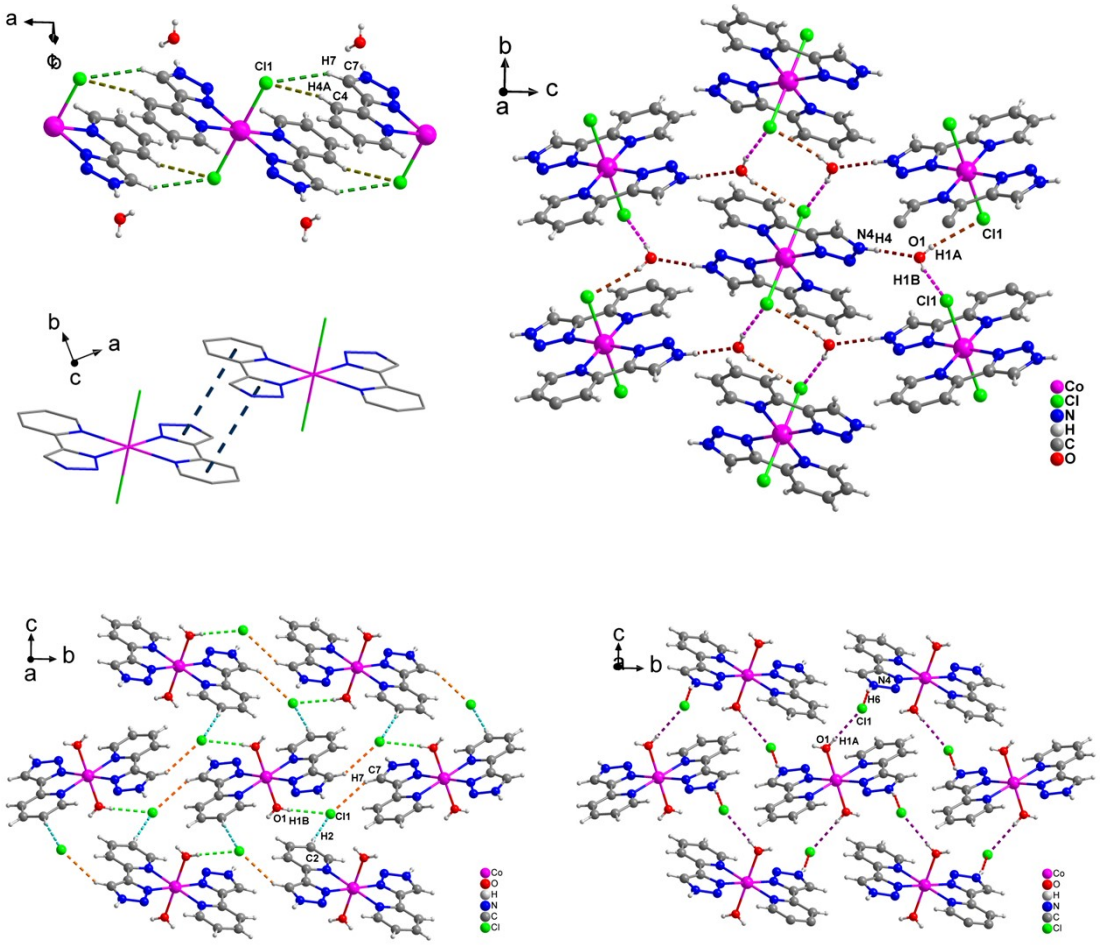


Figure S1 Hydrogen bonding of **Co-Cl** and **Co-H_2O**.

Table S1 Hydrogen bond geometries of **Co-Cl** and **Co-H_2O**.

D	H	A	H···A(Å)	D···A(Å)	D-H···A(°)	Symmetry Operation
Co-Cl						
O1	H1A	Cl1	2.569(32)	3.243(3)	167(3)	x,y,z
O1	H1B	Cl1	2.372(44)	3.138(3)	168(4)	x,2-y,-z
N4	H4	O1	1.900(31)	2.698(3)	174(3)	1/2+x,3/2-y,-1/2+z
Co-H_2O						
O1	H1A	Cl1	2.413(28)	3.147(19)	175(3)	-1/2+x,3/2-y,1/2+z
O1	H1B	Cl1	2.480(31)	3.243(2)	169(3)	1-x,1-y,-z
N4	H4	Cl1	2.238(28)	3.085(2)	167(2)	x,y,z

Time dependent photography

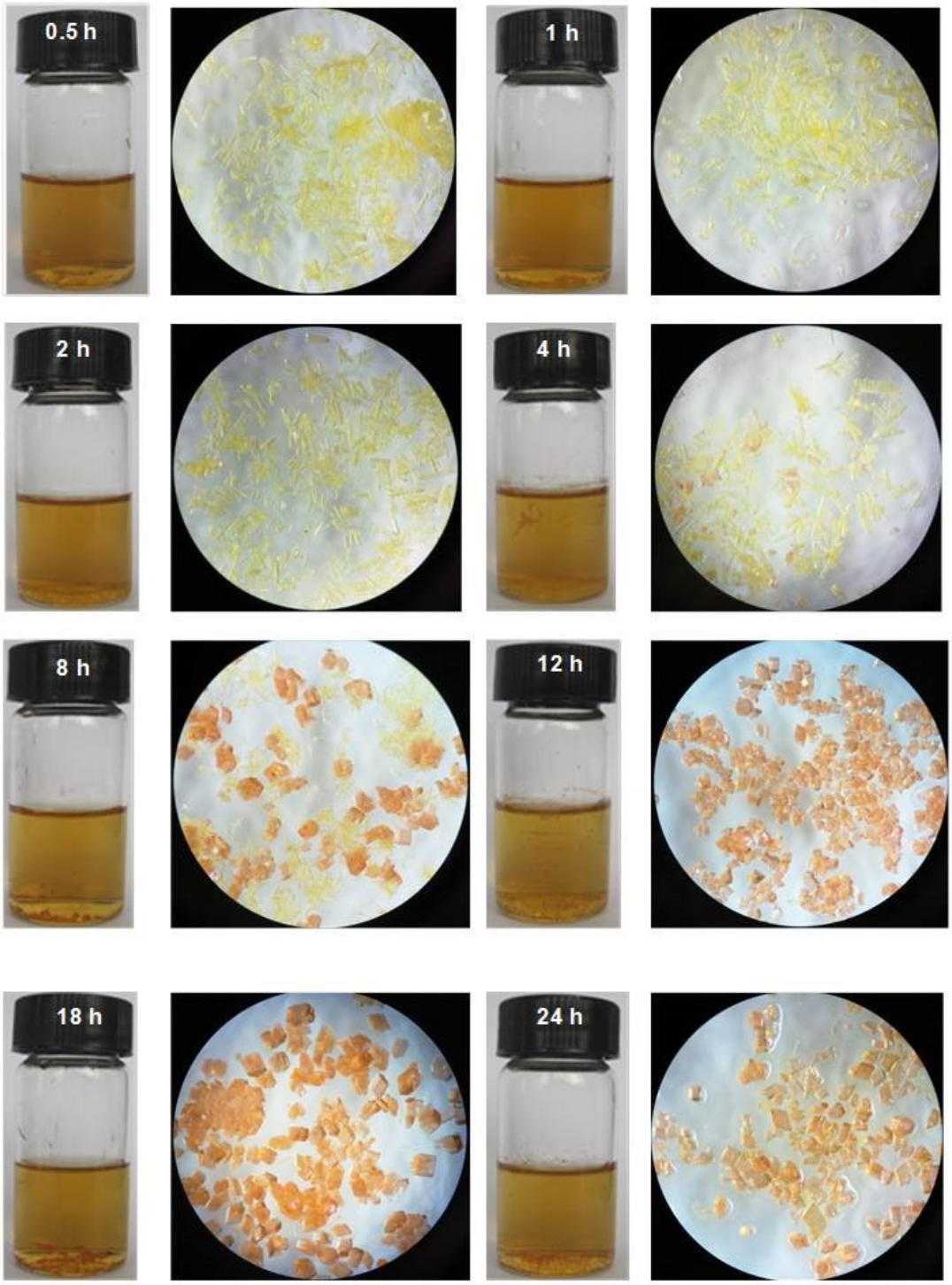


Figure S2 Time dependent photography for solvothermal reaction at 80°C.

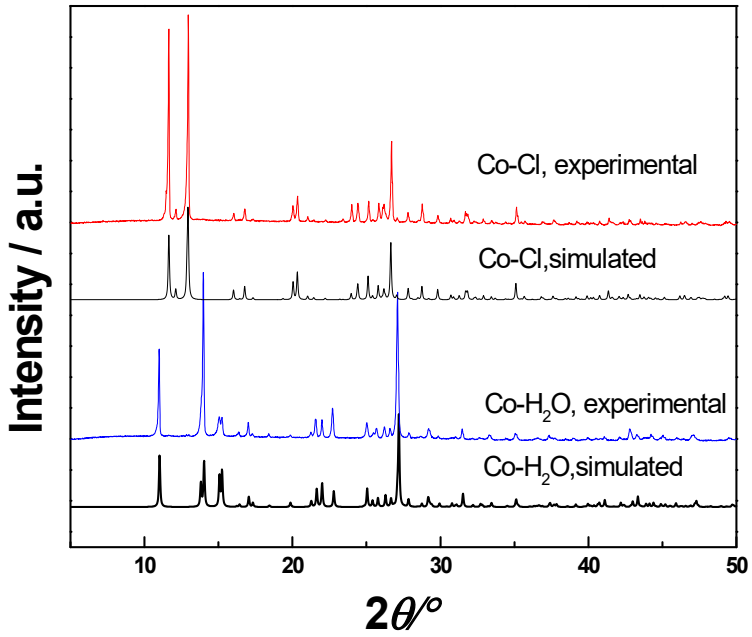


Figure S3 Experimental and simulated PXRD patterns for **Co-Cl** and **Co-H_2O**.

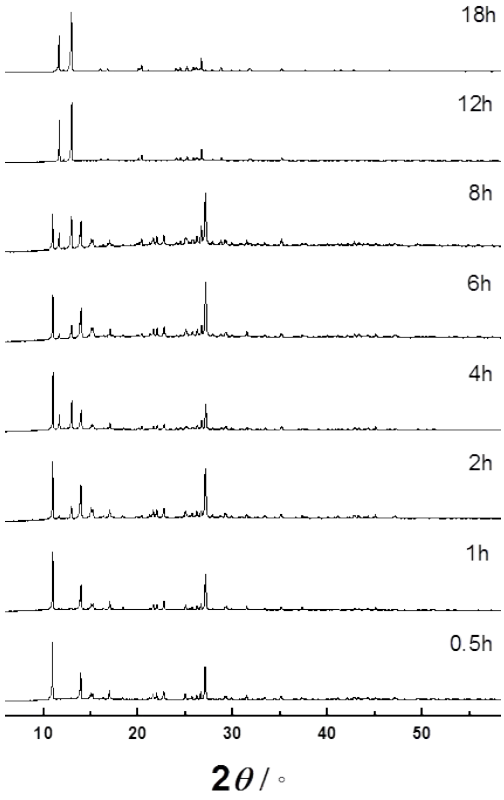


Figure S4 Time dependent powder X-ray pattern for reaction at 80°C.

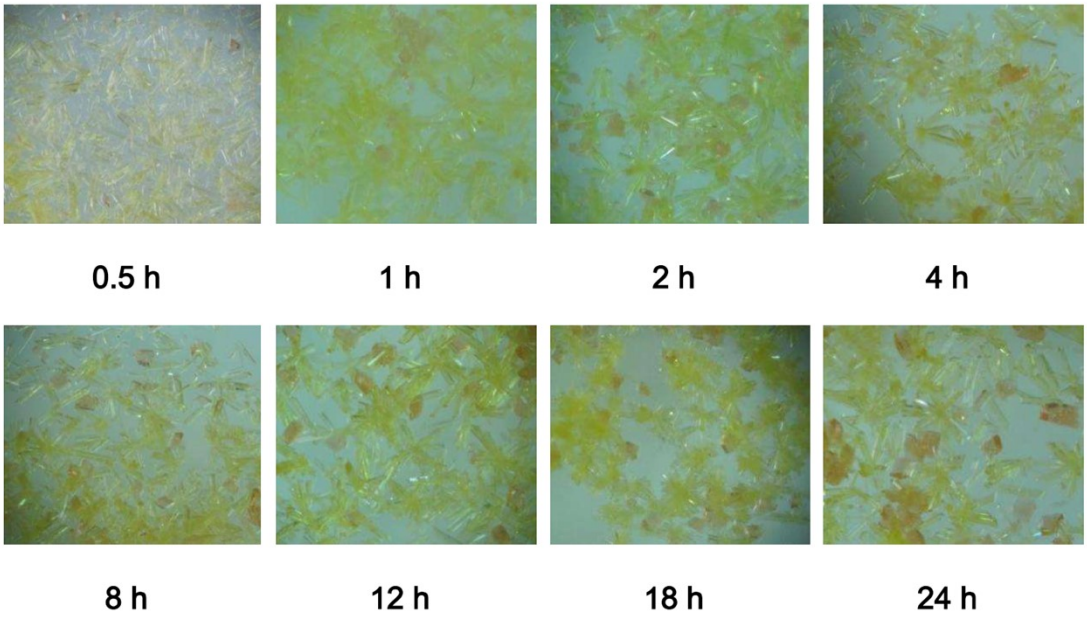


Figure S5 Time dependent photography for solvothermal reaction at 60°C.

ESI-MS

Table S2 Peak assignments of the ESI-MS spectrum (positive mode) of single crystal of **Co-Cl**.

HL=$C_7H_6N_4$

Intensity	m/z	m/z(cal)	fragments
0.52045	147.07	147.07	$[HL+H]^+$
1	175.52	175.53	$\mathbf{[Co(HL)_2]^{2+}}$
0.33225	196.04	196.04	$[Co(CH_3CN)(CH_3OH)_3]^{2+}$
0.00266	204.99	204.99	$[CoL+H]^+$
0.28689	248.55	248.55	$[Co(HL)_3]^{2+}$
0.0255	280.99	280.99	$[Co(HL)(CH_3CN)Cl]^{2+}$
0.01195	286.04	286.04	$[Co\ (HL)\ (CH_3CN)_2]^{2+}$
0.55118	350.04	350.04	$[Co(HL)(L)]^+$
0.12681	386.02	386.02	$\mathbf{[Co(HL)_2Cl]^+}$
0.00598	422.57	422.57	$[Co_2L_3(HL)_2]^{2+}$
6.27E-4	428.06	428.06	$[Co(HL)_2Cl(CH_3CN)H]^+$
0.01355	451.53	451.53	$[Co_3(L)_5H]^{2+}$
0.00107	483.96	483.96	$[Co_2(L)_2Cl(CH_3CN)]^+$
0.13417	495.09	495.09	$[Co_2(L)_2(HL)]^+$
0.01013	553.02	553.02	$[Co_2(L)_3]^{2+}$
0.00148	588.99	589.00	$[Co_2(L)_3ClH]^+$
0.00321	597.08	597.07	$[Co^{III}_2Co^{II}\ (HL)\ (L)_6]^{2+}$
0.006	699.08	699.08	$[Co_2(L)_3(HL)]^+$
0.00288	734.05	734.05	$[Co_2(L)_3(HL)Cl]^+$

0.00129	791.97	791.97	$[Co_3(L)_4Cl]^+$

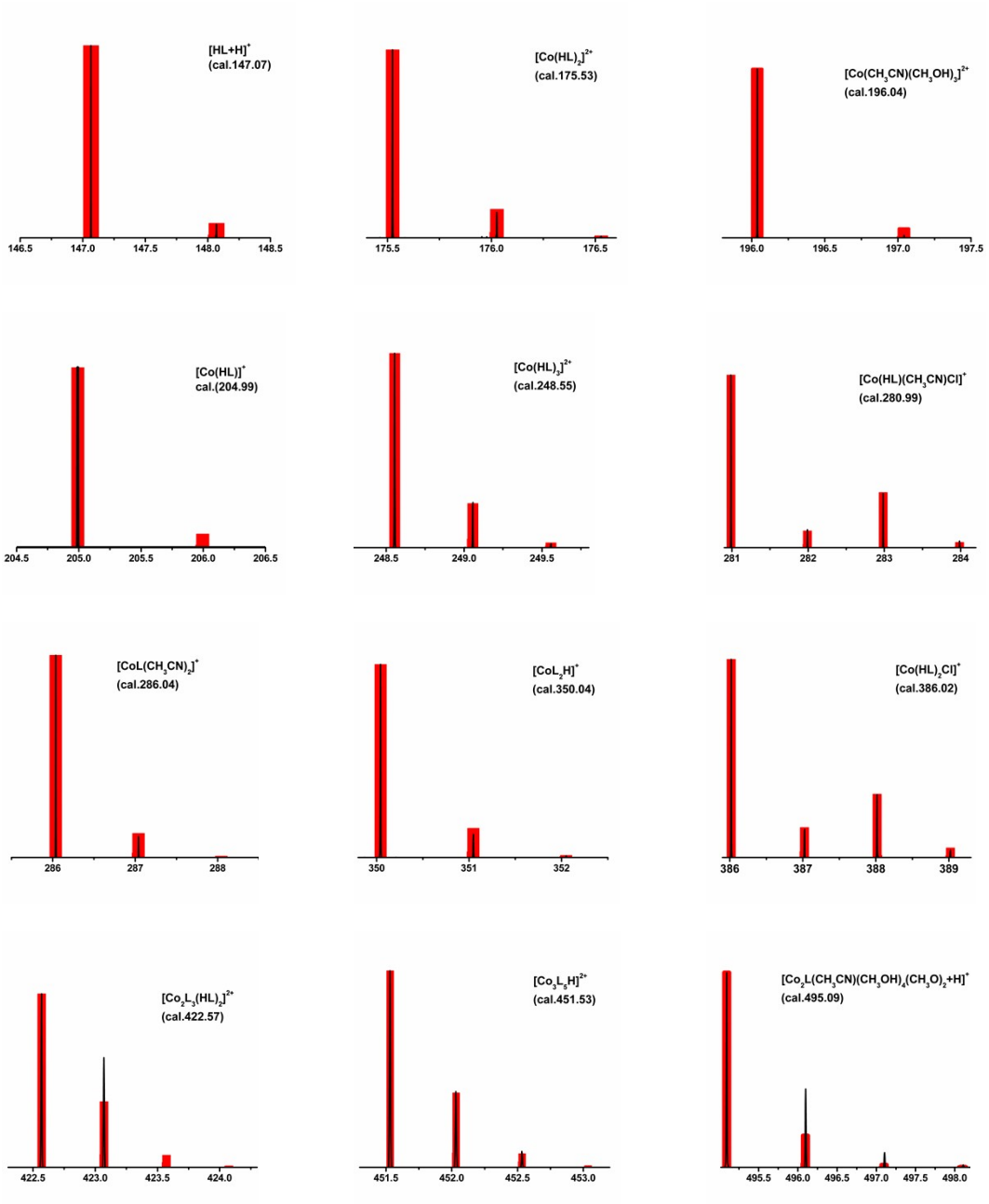


Figure S6 Representation of the calculated peaks fit experimental species present in the ESI-MS spectrum (positive mode) of **Co-Cl**.

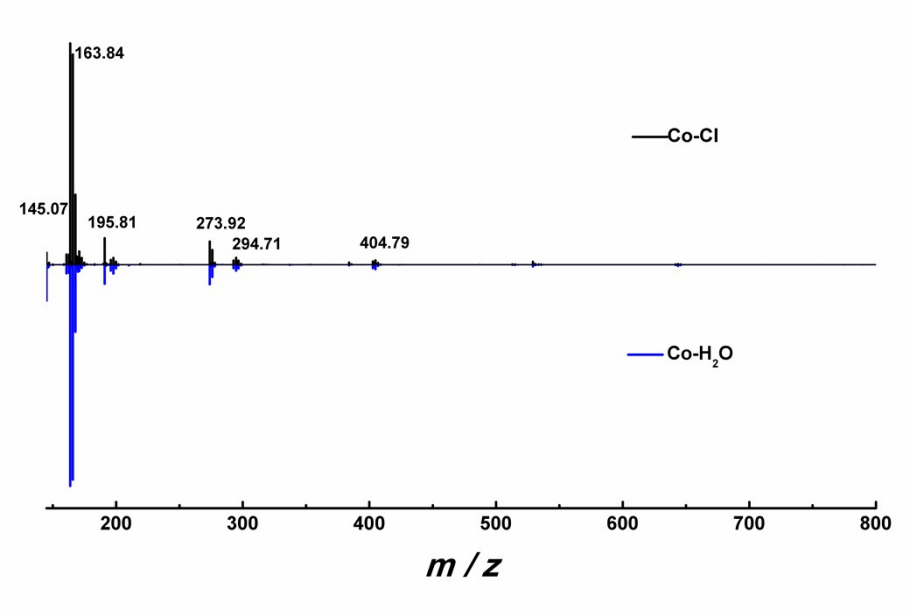


Figure S7 Negative mode ESI-MS of **Co-Cl**.

Table S3 Peak assignments of the ESI-MS spectrum (negative mode) of single crystal of **Co-Cl**.

HL=$C_7H_6N_4$

Intensity	m/z	m/z(cal)	Fragments
0.05606	145.07	145.07	L^-
1	163.84	163.84	$[CoCl_3]^-$
0.10663	273.92	273.92	$[CoLCl_2]^-$
0.03317	294.71	294.71	$[Co_2Cl_5]^-$
0.01137	384.01	384.00	$[CoL_2Cl]^-$
0.02137	404.79	404.79	$[Co_2LCl_4]^-$
9.98099E-4	423.58	423.58	$[Co_3Cl_7]^-$
0.0032523	512.87	512.87	$[Co_2L_2Cl_3]^-$
0.00315	533.66	533.66	$[Co_3LCl_6]^-$
1.37197E-4	622.96	622.96	$[Co_2L_3Cl_2]^-$
1.169E-5	662.53	662.53	$[Co_4LCl_8]^-$
0.00540126	643.74	643.74	$[Co_3L_2Cl_5]^-$
6.26836E-4	753.83	753.83	$[Co_3L_3Cl_4]^-$
4.12906E-4	772.61	772.61	$[Co_4L_2Cl_7]^-$
0.00130819	882.70	882.70	$[Co_4L_3Cl_6]^-$
3.601568E-5	992.78	992.78	$[Co_4L_4Cl_5]^-$

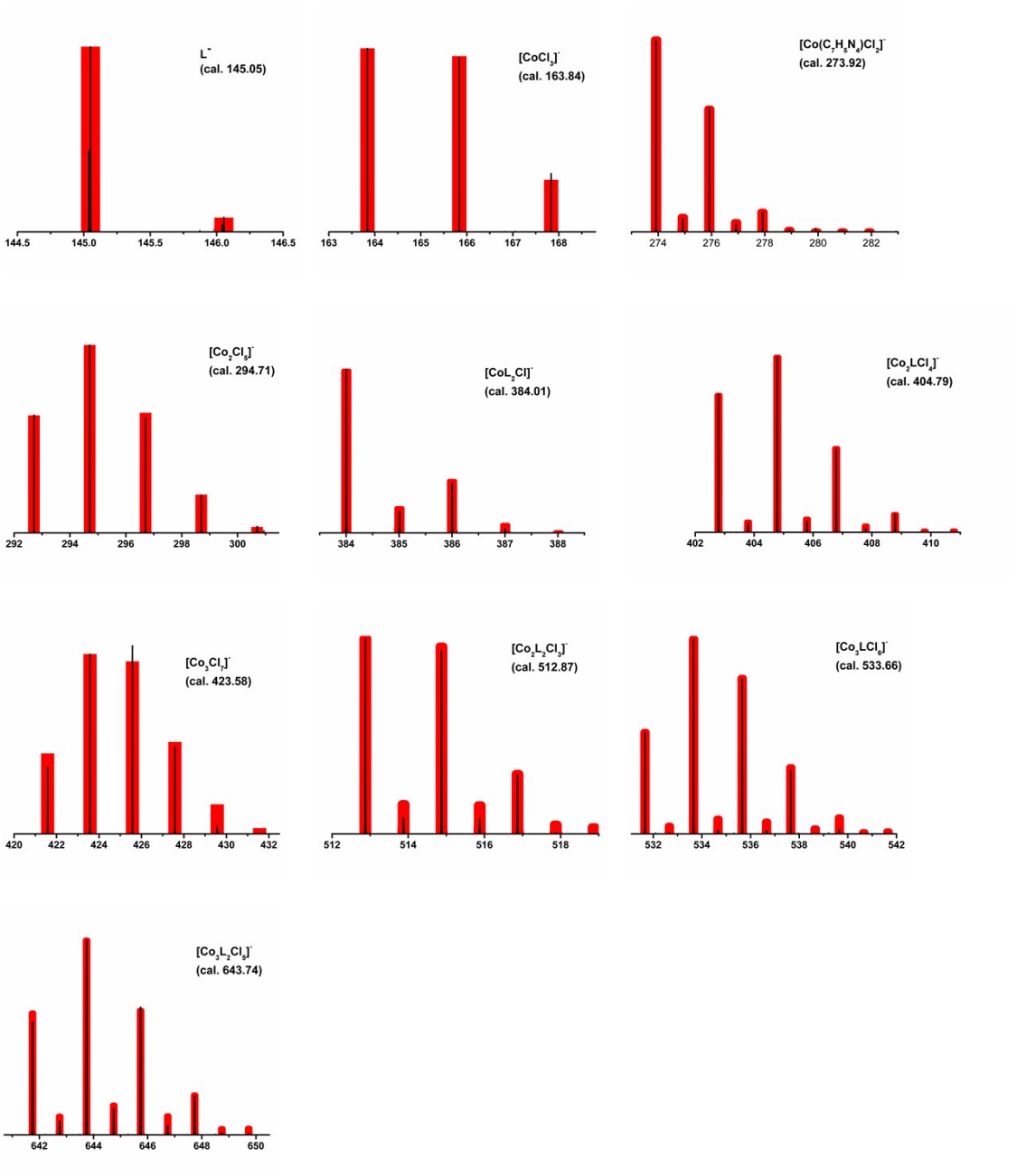


Figure S8 Representation of the calculated peaks fit experimental species present in the ESI-MS spectrum (negative mode) of **Co-Cl**.

Theoretical calculations

Table S4 MS calculated results of **Co-Cl** and **Co-H_2O** crystal.

	Energy type	Total energy
Co-Cl	Crystal	-6865.4339487
	Optimized	-6867.3638070
Co-H_2O	Crystal	-6866.6352352

	Optimized	-6867.3472612

Table S5 Designed species involved in the possible reaction route for forming **Co-Cl** and **Co-H_2O** from $CoCl_2 \cdot 6H_2O$ and ligand.

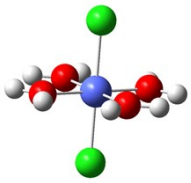
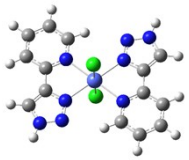
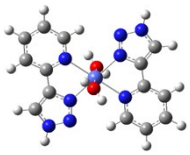
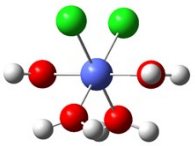
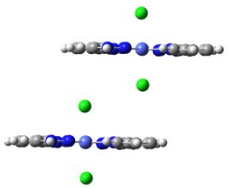
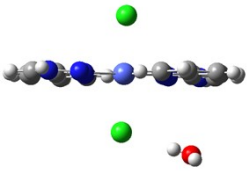
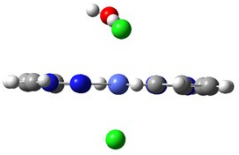
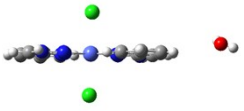
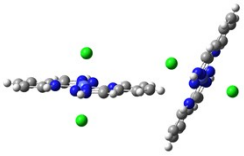
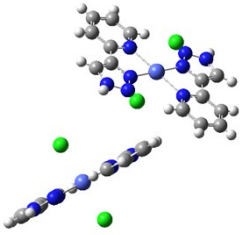
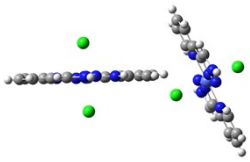
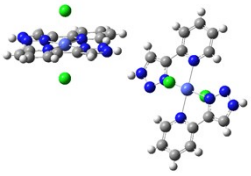
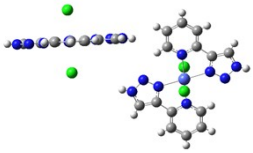
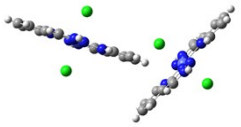
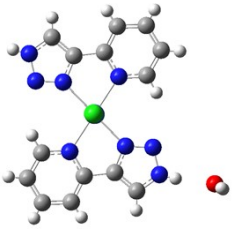
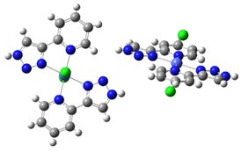
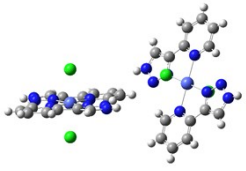
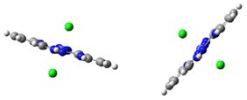
	Reactant	Product 1	Product 2
	 2 L G= -489.347446		
	 CoCl2w4_1	 Co-Cl -2045.200333	 Co-H_2O -1277.214180
	 CoCl2w4_2 -1372.238361		
		 4 water -76.438846	 2 water -76.438846
			 2 Cl- -460.428958
Summary of G (CoCl2w4_2 as reactant)	-2350.933253	-2350.955717	-2350.949788

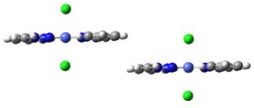
Table S6 Bond order analysis in the optimized complexes of **Co-Cl** and **Co-H_2O**.

	Co-Cl	**Co-H_2O**
Co-Cl/O(w)	0.73742886	0.19343212
Co-N1	0.26582501	0.32380175
Co-N2	0.23380482	0.30608899

Table S7 Calculated complexation energies (kcal/mol) between $[Co(HL)_2Cl_2]\cdot 2H_2O$ monomer and all of its possible neighbors in **Co-Cl** crystals.

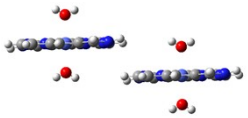
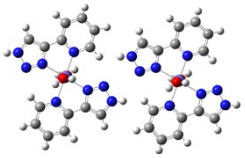
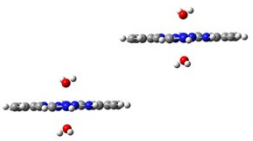
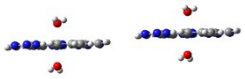
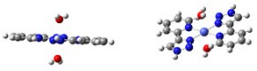
	Co-Cl	Energy a(b)	Interaction Types and Scheme
1	dimer11_14	2.54(3.18)	Cl···Cl (4.599)  O-H···Cl (3.138)
2	dimer11_14	-9.51(-6.91)	 O-H···Cl (3.243)
3	dimer11_14	-7.59(-5.04)	 O-H···Py (3.627)
4	dimer11_14	-1.56(-0.52)	 Cl···Cl (7.156)
5	dimer31_14	-1.31(-0.44)	 Cl···Cl (8.861)
6	dimer32_14	-5.56(-4.97)	
7	dimer34_14	-1.31(-0.44)	Cl···Cl (7.156)

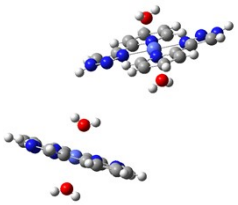
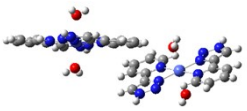
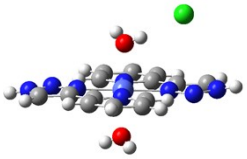
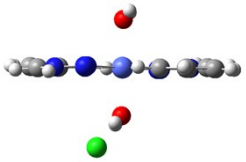
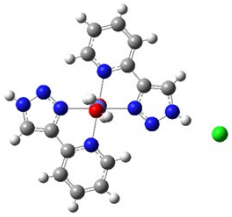
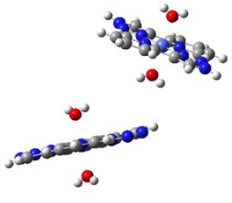
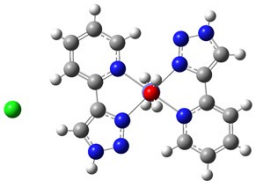
			 Cl···Cl (8.861)
8	dimer35_14	-5.56(-4.97)	 Cl···Cl (8.861)
9	dimer40_14	-5.56(-4.97)	 Cl···Cl (7.156)
10	dimer41_14	-1.31(-0.44)	 N···H_2O (2.698)
11	dimer41_14	-7.66(-5.86)	 Cl···Cl (8.861)
12	dimer43_14	-5.56(-4.97)	 Cl···Cl (7.156)
13	dimer44_14	-1.31(-0.44)	 Cl···Cl (11.548)
14	dimer50_14	0.25(0.26)	
15	dimer5_14	-18.03(-16.09)	Cl···Cl (7.167)

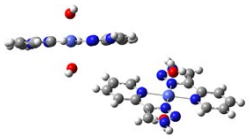
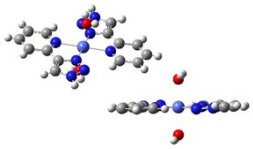
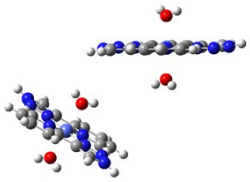
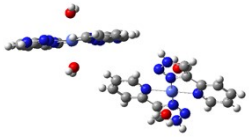
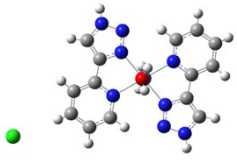
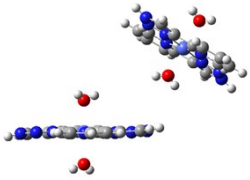
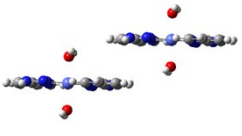
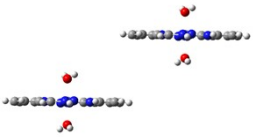
			Cl···Cl (11.081)
16	dimer8_14	-0.98(-0.37)	

[a] Energy without Basis Set Superposition Error (BSSE) correction; [b] Energy after BSSE correction.

Table S8 Calculated complexation energies (kcal/mol) between $[CoL_2(H_2O)_2]\cdot Cl_2$ monomer and all possible neighbors in **Co-H_2O** crystals.

	Co-H_2O	**Energy a(b)**	**Interaction Types and Scheme**
			O···O (8.982)
1	dimer11_14	128.38(128.98)	
			O···O (8.982)
2	dimer17_14	128.38(128.98)	
			O···O (11.631)
3	dimer20_14	90.14(90.15)	
			O···O (12.951)
4	dimer26_14	112.99(113.04)	
			O···O (15.317)
5	dimer29_14	83.81(79.84)	
6	dimer37_14	136.43(134.14)	O···O (5.765)

			 O···O (7.988)
7	dimer38_14	133.96(135.47)	 H_2O···Cl (3.118)
8	dimer40_14	-128.90(-132.01)	 H_2O···Cl (3.141)
9	dimer40_14	-132.71(-131.28)	 N···Cl (3.075)
10	dimer40_14	-126.15(-125.41)	 O···O (5.765)
11	dimer40_14	136.44(138.65)	 Py···Cl (3.675)
12	dimer40_14	-118.04(-117.22)	
13	dimer41_14	133.96(135.47)	O···O (7.988)

			 O···O (7.988)
14	dimer46_14	133.96(135.47)	 O···O (5.765)
15	dimer47_14	136.44(138.65)	 O···O (7.988)
16	dimer49_14	133.96(135.47)	 Py···Cl (3.769)
17	dimer49_14	-105.24(-104.73)	 O···O (5.765)
18	dimer50_14	136.44(134.14)	 O···O (8.494)
19	dimer5_14	145.20(146.27)	 O···O (11.631)
20	dimer8_14	90.14(90.15)	

[a] Energy without Basis Set Superposition Error (BSSE) correction; [b] Energy after BSSE correction.

Crystallographic Data Tables

Table S9 Crysallography data and refinement parameters for **Co-Cl** and **Co-H_2O**.

Compound	$Co[(HL)_2Cl_2]\cdot 2H_2O$	$Co[(HL)_2(H_2O)_2]Cl_2$
CCDC	2177958	2177960
Empirical formula	$C_{14}H_{16}Cl_2CoN_8O_2$	$C_{14}H_{16}Cl_2CoN_8O_2$
Formula weight	458.18	458.18
Temperature	293 K	293 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions	a=8.0159(5) α=90°	a=7.0384(8) α=90°
	b=7.6491(6) β=94.218(6)°	b=10.3897(8) β=95.857(10)
	c=15.2205(11) γ=90°	c=12.6776(11) γ=90°
Volume	930.71(11) $Å^3$	922.25(15) $Å^3$
Z	2	2
Density (calculated)	1.628 g cm^{-3}	1.650 g cm^{-3}
Absorption coefficient	1.237 mm^{-1}	1.249 mm^{-1}
F(000)	462.0	466.0
Theta range for data collection	3.6680 to 30.5240°	3.4570 to 32.8110°
Index ranges	-9<=h<=9	-5<=h<=8
	-9<=k<=5	-12<=k<=12
	-18<=l<=18	-15<=l<=15
Reflections collected	3395	3522
Independent reflections	1548 ([R(int) = 0.0227])	1596 ([R(int) = 0.0205])
Completeness	99.9% (theta = 30.5240˚)	99.2% (theta = 25.970˚)
Goodness-of-fit	1.050	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0925	R1 = 0.0260, wR2 = 0.0632
R indices (all data)	R1 = 0.0429, wR2 = 0.1040	R1 = 0.0326, wR2 = 0.0694

Table S10 Selected bond length(Å) and angles(°) of **Co-Cl**

Bond	Length/Angle	Bond	Length/Angle
Co1—Cl1	2.4744 (7)	Co1—N1	2.1386 (19)
Co1—Cl1^{i}	2.4743 (7)	Co1—N2^{i}	2.1281 (19)
Co1—N1^{i}	2.1385 (19)	Co1—N2	2.1281 (19)
Cl1^{i}—Co1—Cl1	180.0	N2^{i}—Co1—N1	102.56 (7)
N1^{i}—Co1—Cl1^{i}	87.60 (6)	N2^{i}—Co1—N1^{i}	77.44 (7)
N1^{i}—Co1—Cl1	92.40 (6)	N2—Co1—N1	77.43 (7)
N1—Co1—Cl1	87.60 (6)	N2—Co1—N1^{i}	102.57 (7)
N1—Co1—Cl1^{i}	92.40 (6)	N2—Co1—N2^{i}	180.0
N1^{i}—Co1—N1	180.0	C5—N1—Co1	116.09 (15)
N2^{i}—Co1—Cl1	90.64 (6)	C1—N1—Co1	126.08 (17)
N2—Co1—Cl1^{i}	90.64 (6)	N2^{i}—Co1—Cl1^{i}	89.36 (6)
N2—Co1—Cl1	89.36 (6)		

Symmetry code: (i) −x, −y+1, −z.

Table S11 Selected bond length(Å) and angles(°) of **Co-H_2O**

Bond	Length/Angle	Bond	Length/Angle
Co1—O1	2.0962 (17)	Co1—N1	2.1357 (15)
Co1—O1^{i}	2.0962 (17)	Co1—N2^{i}	2.0882 (16)
Co1—N1^{i}	2.1357 (15)	Co1—N2	2.0882 (16)
O1—Co1—O1^{i}	180.0	N2^{i}—Co1—O1^{i}	91.22 (7)
O1^{i}—Co1—N1^{i}	90.17 (7)	N2^{i}—Co1—N1^{i}	77.80 (6)
O1—Co1—N1	90.17 (7)	N2^{i}—Co1—N1	102.20 (6)
O1^{i}—Co1—N1	89.83 (7)	N2—Co1—N1^{i}	102.20 (6)
O1—Co1—N1^{i}	89.83 (7)	N2—Co1—N1	77.80 (6)
N1^{i}—Co1—N1	180.0	N2^{i}—Co1—N2	180.0
N2^{i}—Co1—O1	88.78 (7)	Co1—O1—H1A	120 (2)
N2—Co1—O1^{i}	88.78 (7)	Co1—O1—H1B	124 (2)
N2—Co1—O1	91.22 (7)		

Symmetry code: (i) −*x*, −*y*+1, −*z*.

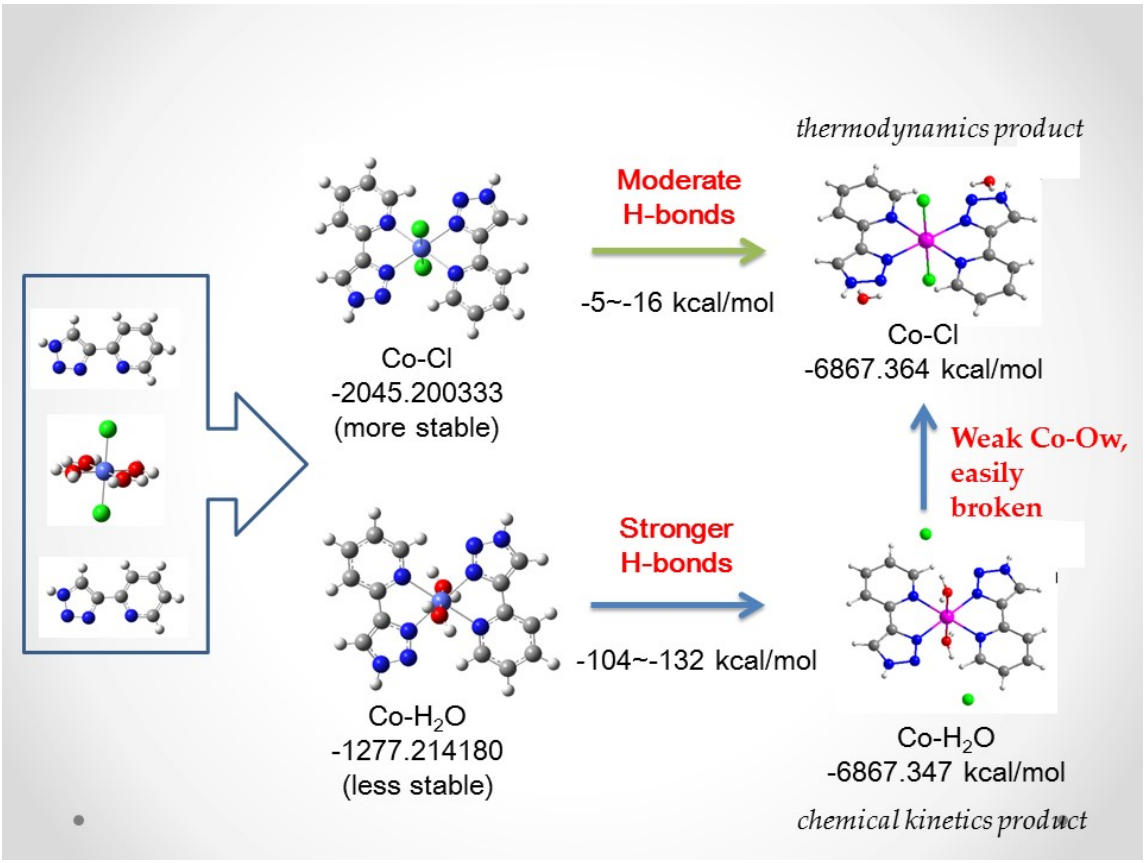


Figure S9 Proposed Formation Process.

UV-vis spectra of Co-Cl and Co-H_2O

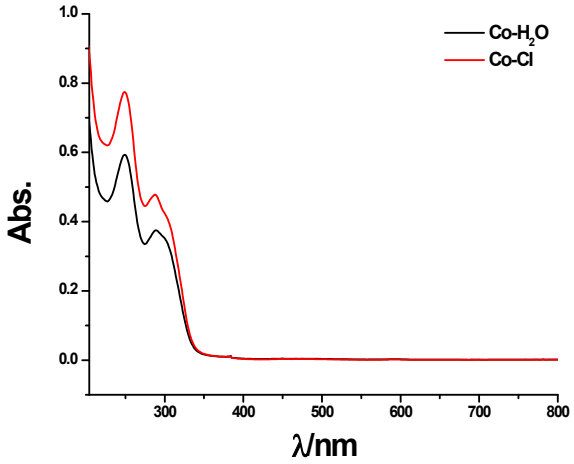


Figure S10 UV-Vis spectra for diluted sample.

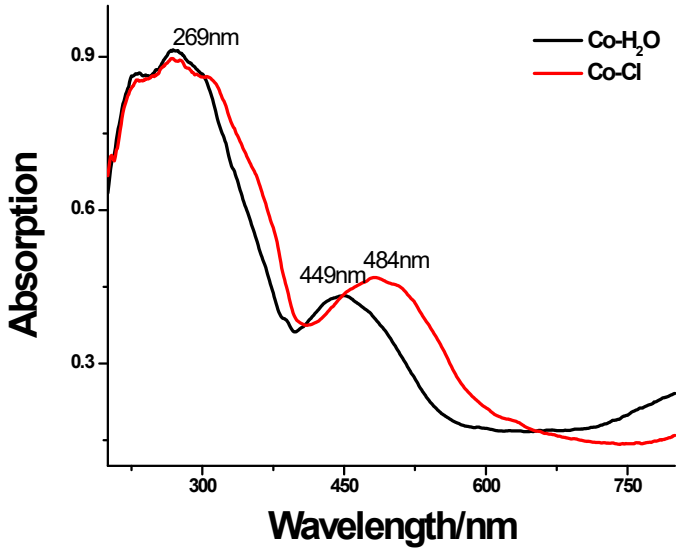


Figure S11 Diffuse reflectance spectroscopy of **Co-Cl** and **Co-H_2O**

IR spectra of Co-Cl and Co-H2O

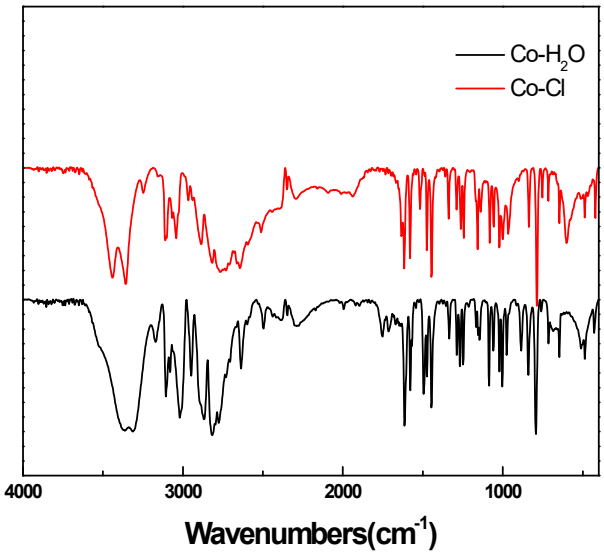


Figure S12 IR spectrum for **Co-Cl** and **Co-H_2O**.