Supporting Information for

Synthesis of Cobalt Cluster-based Supramolecular Triple-Stranded Helicates

Hyojong Yoo[a]* *Jeonghee Lee,*[a] *Philjae Kang,*[b] *Moon-Gun Choi*[b]

[a] Department of Chemistry, Hallym University, Chuncheon, Gangwon-do, 200-702, Republic of Korea
[b] Department of Chemistry, Yonsei University, Seoul, 120-749, Republic of Korea

*Corresponding author.

E-mail address: hyojong@hallym.ac.kr (H. Yoo).

General Methods All glassware was oven-dried prior to use. ^{1}H NMR spectra were obtained at 300 MHz FT-NMR Varian Mercury spectrometer at 303 K. ^{1}H chemical shifts are reported relative to tetramethylsilane. IR spectra of the complexes were recorded in the 399–4000 cm^{-1} range using KBr pellets on a FT/IR-4200 JASCO spectrometer. Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT Q600 analyzer under a nitrogen atmosphere from 18 to 600 °C at a heating rate of 2 °C/min. Powder X-ray diffraction (PXRD) analysis was performed on a RIGAKU Ultima IV diffractometer using Cu Kα radiation (wavelength 1.541 Å) in focused beam configuration with a continuous scan rate of 4° min^{-1} in the 3-80° range. Simulated PXRD patterns were calculated from single crystal X-ray diffraction data using the Mercury 3.3 program. Ultraviolet-visible-near infrared (UV-vis-NIR) spectra were recorded on a UV-3200 Shimadzu spectrophotometer. Elemental analyses were performed on a Thermo Finnigan Flash EA1112 unit. Circular dichroism (CD) analysis was performed on a J-815 JASCO spectrometer.

Materials Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 98 %, Sigma-Aldrich), cobalt(II) acetate tetrahydrate ($Co(OAc)_2 \cdot 4H_2O$, ≥98 %, Sigma-Aldrich), 2,6-pyridinedicarboxylic acid ($C_7H_5NO_4$, 99%, Sigma-Aldrich), benzene-1,3-dicarboxylic acid ($C_8H_6O_4$, 99%, Sigma-Aldrich), N,N-dimethylformamide (DMF, 99.99%, Burdick & Jackson), dimethyl sulfoxide (DMSO, 99.0%, Samchun), and HCl (extra pure, Burdick & Jackson) were used as received. $CDCl_3$ (99.8%, +0.05% TMS, Cambridge Isotope Laboratories, Inc.) and DMSO-d_6 (99.9%, Cambridge Isotope Laboratories, Inc.) were used as received. Abbreviations used: OAc = acetate, PDA = 2,6-pyridinedicarboxylate, H_2PDA = 2,6-pyridinedicarboxylic acid, PTA = benzene-1,3-

dicarboxylate (common name: isophthalate), H_2PTA = benzene-1,3-dicarboxylic acid (common name: isophthalic acid).

Synthesis of $Co_8(PDA)_6(PTA)_3(DMF)_3(H_2O)_3$ (1) $Co(NO_3)_2{\cdot}6H_2O$ (11.64 mg, 0.04 mmol), H_2PDA (3.34 mg, 0.02 mmol), H_2PTA (3.32 mg, 0.02 mmol), HCl (0.1mL, 0.01mmol), and DMF (1.599 mL, 20.8 mmol) were mixed in a vial at room temperature. The vial was sealed tightly, and heated to 120 °C in an oven. Crystals began to form after 3 h at 120 °C. To reach completion, the reaction mixture was kept at 120 °C for 48 h, and then cooled to room temperature. Purple needle-shaped crystals were collected, washed with DMF (3 × 4 mL) and acetone (2 × 2 mL), and dried; the yield was 48.7 % (crystals yield; based on the amount of H_2PDA used). Strong absorption bands in the FT-IR spectrum of **1** at ~3379 cm^{-1} are attributed to ν(O-H); a peak at ~1622 cm^{-1} corresponds to the deformation vibration of the water molecules. Bands between 3300 and 2700 cm^{-1} appear bands (2933, 2805 cm^{-1}) corresponds to ν(C-H)s. Anal. Calcd. for $C_{75}H_{57}Co_8N_9O_{42}{\cdot}3DMF{\cdot}H_2O$: C, 40.93; H, 3.33; N, 6.82, Found: C, 40.83; H, 3.32; N, 7.08

Synthesis of $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–0.51(Co(OH_n)_2)]$ (2) $Co(OAc)_2{\cdot}4H_2O$ (37.4 mg, 0.15 mmol), H_2PDA (10.0 mg, 0.06 mmol), H_2PTA (5 mg, 0.03 mmol), DMSO (0.1mL, 1.4 mmol), and DMF (2.4 mL, 31.2 mmol) were mixed in a vial at room temperature. The vial was sealed tightly and then heated to 120°C (increasing rate; 3°C/min). Crystals began to form after 3 h at 120 °C. To reach completion, the reaction mixture was kept at 120 °C for 48 h, and then cooled to room temperature. Purple needle-shaped crystals were collected, washed with DMF (3 × 4 mL), acetone (2 × 2 mL) and dried; the yield was 44.5 % (crystals yield; based on H_2PDA

used). Anal. Calcd. for $C_{72}H_{52}Co_{8.52}N_8O_{43}\cdot 3DMF$: C, 39.89; H, 3.02; N, 6.32, Found: C, 40.048; H, 2.2889; N, 6.169.

Single crystal X-ray diffraction analysis of $Co_8(PDA)_6(PTA)_3(DMF)_3(H_2O)_3$ (1) A specimen of suitable size and quality was coated with Paratone oil and mounted on a MiTeGen MicroMount©. Reflection data were collected on a Bruker D8 Venture PHOTON 100 area detector diffractometer, with Cu K_α radiation (λ = 1.54178 Å). The full sphere of reflection data was collected as ω and φ scan frames at 1°/frame and an exposure time of 30 s/frame. Cell parameters were determined and refined by the APEX2 program.[1] Data reduction was performed using the SAINT software.[2] The data were corrected for Lorentz and polarization effects. Empirical absorption correction was applied using the SADABS program.[3] The structure was solved by direct methods and all nonhydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL and Olex 2 GUI program.[4] Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The voids contained disordered DMF with a partial occupancy. A satisfactory disorder model for the solvent was not found, therefore the Olex2 Solvent Mask routine was used to mask out the disordered density. The masked electron density of 156.3 e- per unit cell could be interpreted as 4 DMFs (160 e-). One of PDA ligands (C30-C36) was found to be disordered and was modeled in two different orientations using the restraints of RIGU, FLAT and ISOR. The partial occupancy of both orientations was fixed to 0.5. The substitutionally disordered solvent molecules (water, DMF), which are coordinated to Co4 were treated with a partial occupancy of 0.5.

Single crystal X-ray diffraction analysis of [$Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4$–0.51 ($Co(OH_n)_2$)] A specimen of suitable size and quality was coated with Paratone oil and mounted on a MiTeGen MicroMount©. Reflection data were collected on a Bruker D8 Venture PHOTON 100 area detector diffractometer, with Cu K_α radiation (λ = 1.54178 Å). The full sphere of reflection data was collected as ω and φ scan frames with 1°/frame and an exposure time of 20 s/frame. Cell parameters were determined and refined by the APEX2 program.[1] Data reduction was performed using SAINT software.[2] The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program.[3] The structure was solved by direct methods, and all nonhydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL and Olex 2 GUI program.[4] Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Co5 has non-stoichiometric occupancy (0.51). The voids contained disordered DMF with a partial occupancy. A satisfactory disorder model for the solvent was not found, and therefore the Olex2 Solvent Mask routine was used to mask out disordered density. The masked electron density of 329.5 e^- per unit cell could be interpreted as 8 DMF (320 e^-). The restrain of ISOR was used to treat the disordered atoms of C32, C33, O19, and C40. The solvent molecules (DMF, H_2O), which were coordinated to Co4 were extremely disordered and modeled in two different orientation with fixed partial occupancy of 0.5. Although high electron density on the outer side of the O(20) and O(20A) was observed, further treatments for disordered DMF molecules were unsuccessful.

Table S1. Crystallographic Data for $Co_8(PDA)_6(PTA)_3(DMF)_3(H_2O)_3$, **1** and $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–0.51(Co(OH_n)_2)]$, **2**.

	1	**2**
Empirical formula	$C_{72}H_{57}Co_8N_9O_{42}$	$C_{76.28}H_{62}Co_{8.51}N_{9.43}O_{44.45}$
Formula weight	2227.73	2323.66
Temperature/K	120.0	100.0
Crystal system	Trigonal	trigonal
Space group	$P3_121$	$P3_121$
a/Å	23.945(2)	23.9077(5)
b/Å	23.945(2)	23.9077(5)
c/Å	17.1792(16)	17.2642(5)
α/°	90	90
β/°	90	90
γ/°	120	120
Volume/Å^3	8530.6(18)	8545.8(4)
Z	3	3
ρ_{calc}mg/mm^3	1.301	1.355
m/mm^{-1}	1.212	10.158
F(000)	3366.0	3514.0
Crystal size/mm^3	0.41 × 0.091 × 0.066	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2Θ range for data collection	5.838 to 50.968	6.666 to 145.148
Index ranges	-28 ≤ h ≤ 28, -28 ≤ k ≤ 28, -20 ≤ l ≤ 20	-29 ≤ h ≤ 29, -29 ≤ k ≤ 29, -21 ≤ l ≤ 20
Reflections collected	78659	147932
Independent reflections	10527 [R(int) = 0.0799, R(sigma)=0.0408]	11216 [R(int) = 0.1243, R(sigma) = 0.0546]
Data/restraints/parameters	10527/810/679	11216/297/663
Goodness-of-fit on F^2	1.082	1.095
Final R indexes [I>=2σ (I)]	R_1 = 0.0578, wR_2 = 0.1562	R_1 = 0.0729, wR_2 = 0.2014
Final R indexes [all data]	R_1 = 0.0760 wR_2 = 0.1700	R_1 = 0.0830, wR_2 = 0.2107
Largest diff. peak/hole / e Å^{-3}	0.71/-0.46	1.38/-0.61
Flack parameter	-0.008(6)	0.013(3)

Table S2. Bond Distances (Å) in $Co_8(PDA)_6(PTA)_3(DMF)_3(H_2O)_3$, **1** [a]

Co1-O1	2.128(6)	O22-C40	1.20(4)
Co1-O5	2.086(6)	N1-C1	1.333(11)
Co1-O9	2.116(6)	N1-C5	1.316(11)
Co1-O13	2.029(6)	N2-C8	1.312(12)
Co1-O15[1]	2.038(6)	N2-C12	1.342(11)
Co1-O17A	2.11(2)	N3-C15	1.321(14)
Co2-O1	2.286(6)	N3-C19	1.385(13)
Co2-O3	2.106(6)	N4-C37	1.275(13)
Co2-O10	2.109(7)	N4-C38	1.454(13)
Co2-O16[1]	2.035(6)	N4-C39	1.438(14)
Co2-O20	2.146(6)	N5-C40	1.46(4)
Co2-N1	2.063(7)	N5-C41	1.15(3)
Co3-O2	2.085(6)	N5-C42	1.51(4)
Co3-O5	2.248(6)	C1-C2	1.374(13)
Co3-O7	2.111(6)	C1-C6	1.494(13)
Co3-O14	1.999(6)	C2-C3	1.348(14)
Co3-O19	2.128(8)	C3-C4	1.420(14)
Co3-N2	2.062(7)	C4-C5	1.358(13)
Co4-O6	2.118(7)	C5-C7	1.490(13)
Co4-O9	2.238(7)	C8-C9	1.389(12)
Co4-O11	2.138(8)	C8-C13	1.492(12)
Co4-O18A	2.09(2)	C9-C10	1.403(14)
Co4-O21	2.14(2)	C10-C11	1.344(13)
Co4-O22	2.03(2)	C11-C12	1.390(12)
Co4-N3	2.022(9)	C12-C14	1.503(13)
O1-C6	1.255(10)	C15-C16	1.363(14)
O2-C6	1.290(10)	C15-C20	1.498(14)
O3-C7	1.275(11)	C16-C17	1.367(17)
O4-C7	1.249(11)	C17-C18	1.375(18)
O5-C13	1.301(11)	C18-C19	1.334(15)
O6-C13	1.231(11)	C19-C21	1.506(18)
O7-C14	1.262(10)	C22-C23	1.375(12)
O8-C14	1.241(11)	C22-C27	1.395(13)
O9-C20	1.276(11)	C22-C28	1.508(12)
O10-C20	1.247(12)	C23-C24	1.406(12)
O11-C21	1.236(14)	C24-C25	1.385(12)
O12-C21	1.193(16)	C24-C29	1.500(11)
O13-C28	1.242(10)	C25-C26	1.385(12)
O14-C28	1.258(10)	C26-C27	1.373(13)
O15-Co1[1]	2.038(6)	C30-C31	1.39
O15-C29	1.245(10)	C30-C35	1.39

O16-Co2[1]	2.035(6)	C30-C36A	1.47(3)
O16-C29	1.252(11)	C31-C32	1.39
O17-C36	1.13(4)	C32-C33	1.39
O17A-C36A	1.38(4)	C33-C34	1.39
O18-C36	1.30(4)	C34-C35	1.39
O18A-C36A	1.27(3)	C34-C36	1.51(3)
O20-C37	1.236(11)		

[1]1-Y+X,2-Y,2/3-Z; [2]+Y,+X,-Z

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] "A" show the atoms from disordered phenyl groups.

Table S3. Bond Angles (deg) in $Co_8(PDA)_6(PTA)_3(DMF)_3(H_2O)_3$, **1** [a]

O5-Co1-O1	89.2(2)	C8-N2-C12	122.4(8)
O5-Co1-O9	88.0(2)	C12-N2-Co3	116.5(6)
O5-Co1-O17A	97.8(8)	C15-N3-Co4	122.5(7)
O9-Co1-O1	88.3(2)	C15-N3-C19	118.2(9)
O13-Co1-O1	96.1(2)	C19-N3-Co4	119.2(7)
O13-Co1-O5	90.2(2)	C37-N4-C38	120.1(8)
O13-Co1-O9	175.2(3)	C37-N4-C39	124.6(9)
O13-Co1-O151	88.3(2)	C39-N4-C38	115.3(9)
O13-Co1-O17A	85.2(6)	C40-N5-C42	117(2)
O151-Co1-O1	86.7(2)	C41-N5-C40	119(3)
O151-Co1-O5	175.5(3)	C41-N5-C42	120(3)
O151-Co1-O9	93.9(2)	N1-C1-C2	121.3(9)
O151-Co1-O17A	86.3(7)	N1-C1-C6	112.8(8)
O17A-Co1-O1	172.8(8)	C2-C1-C6	125.9(9)
O17A-Co1-O9	90.7(6)	C3-C2-C1	119.4(10)
O3-Co2-O1	150.0(2)	C2-C3-C4	118.4(9)
O3-Co2-O10	93.8(3)	C5-C4-C3	118.7(9)
O3-Co2-O20	91.1(3)	N1-C5-C4	121.4(9)
O10-Co2-O1	85.1(2)	N1-C5-C7	112.8(8)
O10-Co2-O20	175.1(2)	C4-C5-C7	125.6(8)
O161-Co2-O1	112.4(2)	O1-C6-O2	123.9(8)
O161-Co2-O3	97.6(3)	O1-C6-C1	118.5(8)
O161-Co2-O10	88.1(3)	O2-C6-C1	117.4(8)
O161-Co2-O20	91.1(2)	O3-C7-C5	116.7(8)
O161-Co2-N1	172.8(3)	O4-C7-O3	124.3(9)
O20-Co2-O1	90.8(2)	O4-C7-C5	119.0(8)
N1-Co2-O1	73.7(2)	N2-C8-C9	119.7(8)
N1-Co2-O3	76.3(3)	N2-C8-C13	114.7(8)
N1-Co2-O10	88.5(3)	C9-C8-C13	125.5(8)
N1-Co2-O20	92.8(3)	C8-C9-C10	118.8(9)
O2-Co3-O5	88.9(2)	C11-C10-C9	119.8(9)
O2-Co3-O7	89.4(3)	C10-C11-C12	119.3(9)
O2-Co3-O19	176.3(3)	N2-C12-C11	119.9(8)
O7-Co3-O5	151.1(2)	N2-C12-C14	113.0(7)
O7-Co3-O19	92.9(3)	C11-C12-C14	127.0(8)
O14-Co3-O2	90.0(3)	O5-C13-C8	115.4(8)
O14-Co3-O5	107.8(2)	O6-C13-O5	126.6(8)

O14-Co3-O7	101.0(2)	O6-C13-C8	118.0(8)
O14-Co3-O19	86.7(3)	O7-C14-C12	117.3(8)
O14-Co3-N2	174.3(3)	O8-C14-O7	126.1(9)
O19-Co3-O5	90.5(3)	O8-C14-C12	116.5(8)
N2-Co3-O2	95.5(3)	N3-C15-C16	121.0(10)
N2-Co3-O5	74.1(3)	N3-C15-C20	112.4(8)
N2-Co3-O7	77.4(3)	C16-C15-C20	126.6(10)
N2-Co3-O19	87.9(3)	C15-C16-C17	119.4(12)
O6-Co4-O9	86.5(2)	C16-C17-C18	121.0(11)
O6-Co4-O11	91.0(3)	C19-C18-C17	116.7(12)
O6-Co4-O21	172.2(5)	N3-C19-C21	110.9(10)
O11-Co4-O9	149.6(3)	C18-C19-N3	123.4(11)
O11-Co4-O21	95.9(6)	C18-C19-C21	125.6(11)
O18A-Co4-O6	81.5(6)	O9-C20-C15	116.7(9)
O18A-Co4-O9	116.5(6)	O10-C20-O9	126.1(9)
O18A-Co4-O11	93.1(6)	O10-C20-C15	117.2(8)
O21-Co4-O9	85.7(5)	O11-C21-C19	115.9(11)
O22-Co4-O6	172.8(6)	O12-C21-O11	127.2(14)
O22-Co4-O9	100.5(6)	O12-C21-C19	116.9(12)
O22-Co4-O11	82.1(6)	C23-C22-C27	119.4(8)
O22-Co4-O18A	96.8(9)	C23-C22-C28	120.7(8)
N3-Co4-O6	90.8(3)	C27-C22-C28	119.8(8)
N3-Co4-O9	74.2(3)	C22-C23-C24	121.2(8)
N3-Co4-O11	75.5(3)	C23-C24-C29	119.8(8)
N3-Co4-O18A	166.1(6)	C25-C24-C23	118.1(8)
N3-Co4-O21	87.5(7)	C25-C24-C29	122.0(8)
N3-Co4-O22	89.4(7)	C26-C25-C24	120.6(8)
Co1-O1-Co2	104.0(2)	C27-C26-C25	120.6(8)
C6-O1-Co1	137.6(6)	C26-C27-C22	119.9(8)
C6-O1-Co2	113.3(5)	O13-C28-O14	125.5(8)
C6-O2-Co3	128.7(6)	O13-C28-C22	117.7(7)
C7-O3-Co2	116.0(6)	O14-C28-C22	116.8(8)
Co1-O5-Co3	106.9(3)	O15-C29-O16	126.2(8)
C13-O5-Co1	136.4(6)	O15-C29-C24	117.0(8)
C13-O5-Co3	114.6(5)	O16-C29-C24	116.8(8)
C13-O6-Co4	128.8(6)	C31-C30-C35	120
C14-O7-Co3	115.6(6)	C31-C30-C36A	116.1(16)
Co1-O9-Co4	105.6(3)	C35-C30-C36A	121.0(16)
C20-O9-Co1	136.5(6)	C30-C31-C32	120

C20-O9-Co4	114.2(6)	C31-C32-C33	120
C20-O10-Co2	126.2(6)	C34-C33-C32	120
C21-O11-Co4	118.0(8)	C33-C34-C36	120.0(17)
C28-O13-Co1	137.0(6)	C35-C34-C33	120
C28-O14-Co3	121.2(6)	C35-C34-C36	118.8(18)
C29-O15-Co11	131.3(6)	C34-C35-C30	120
C29-O16-Co21	113.0(5)	O17-C36-O18	110(3)
C36A-O17A-Co1	122(2)	O17-C36-C34	133(3)
C36A-O18A-Co4	107.2(18)	O18-C36-C34	116(3)
C37-O20-Co2	126.1(6)	O17A-C36A-C30	109(2)
C40-O22-Co4	129(2)	O18A-C36A-O17A	136(3)
C1-N1-Co2	121.4(6)	O18A-C36A-C30	115(2)
C5-N1-Co2	118.1(6)	O20-C37-N4	128.9(10)
C5-N1-C1	120.4(8)	O22-C40-N5	119(3)
C8-N2-Co3	120.8(6)		

[1]1-Y+X,2-Y,2/3-Z; [2]+Y,+X,-Z

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] "A" show the atoms from disordered phenyl groups.

Table S4. Bond Distances (Å) in $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–0.51(Co(OH_n)_2)]$, **2** [a]

Co1-O1	2.138(6)	N1-C1	1.344(11)
Co1-O5	2.154(6)	N1-C5	1.332(11)
Co1-O9	2.102(6)	N2-C8	1.331(13)
Co1-O13	2.049(6)	N2-C12	1.343(12)
Co1-O15	2.043(6)	N3-C15	1.320(13)
Co1-O17	2.050(6)	N3-C19	1.331(12)
Co2-O1	2.278(6)	N4-C35	1.330(14)
Co2-O3	2.111(6)	N4-C36	1.425(14)
Co2-O6	2.118(6)	N4-C37	1.479(16)
Co2-O14	2.020(6)	C1-C2	1.381(12)
Co2-O21	2.131(6)	C1-C6	1.512(12)
Co2-N1	2.055(7)	C2-C3	1.382(15)
Co3-O5	2.232(7)	C3-C4	1.391(16)
Co3-O7	2.197(8)	C4-C5	1.381(13)
Co3-O10	2.088(8)	C5-C7	1.541(12)
Co3-O18	2.002(8)	C8-C9	1.385(13)
Co3-O19	2.052(10)	C8-C13	1.524(12)
Co3-N2	2.051(8)	C9-C10	1.376(15)
Co4-O2	2.071(6)	C10-C11	1.339(17)
Co4-O9	2.244(6)	C11-C12	1.400(14)
Co4-O11	2.109(7)	C12-C14	1.507(15)
Co4-O16	1.997(6)	C15-C16	1.381(12)
Co4-O20	2.124(17)	C15-C20	1.504(13)
Co4-O20A	2.199(16)	C16-C17	1.388(15)
Co4-N3	2.050(7)	C17-C18	1.422(15)
Co5-O7	2.146(8)	C18-C19	1.379(12)
Co5-O71	2.146(8)	C19-C21	1.521(14)
Co5-O22	1.980(16)	C22-C23	1.422(12)
Co5-O22[1]	1.980(16)	C22-C27	1.352(12)
O1-C6	1.261(10)	C22-C28	1.532(11)
O2-C6	1.228(10)	C23-C24	1.411(11)
O3-C7	1.256(11)	C24-C25	1.375(13)
O4-C7	1.216(11)	C24-C29	1.501(12)
O5-C13	1.274(11)	C25-C26	1.367(13)
O6-C13	1.233(11)	C26-C27	1.380(12)
O7-C14	1.261(14)	C29-O15[2]	1.248(12)
O8-C14	1.236(16)	C29-O16[2]	1.267(11)
O9-C20	1.271(11)	C30-C31	1.383(19)
O10-C20	1.256(12)	C30-C33	1.43(2)
O11-C21	1.284(10)	C30-C34	1.523(16)
O12-C21	1.223(12)	C31-C30[2]	1.383(19)

O13-C28	1.223(11)	C32-C33[2]	1.427(18)
O14-C28	1.279(10)	C32-C33	1.427(18)
O15-C29[2]	1.248(12)	O23-C38	1.07(3)
O16-C29[2]	1.267(11)	N5-C38	1.14(3)
O17-C34	1.240(14)	N5-C39	1.57(3)
O18-C34	1.230(14)	N5-C40	1.34(3)
O21-C35	1.270(13)		

[1]1-Y+X,2-Y,2/3-Z; [2]+Y,+X,-Z

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] "A" show the atoms from disordered coordinated water molecule.

Table S5. Bond Angles (deg) in $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–0.51(Co(OH_n)_2)]$, **2** [a]

O1-Co1-O5	89.0(3)	C29[2]-O16-Co4	120.7(6)
O9-Co1-O1	88.8(2)	C34-O17-Co1	135.7(8)
O9-Co1-O5	88.3(2)	C34-O18-Co3	116.9(8)
O13-Co1-O1	85.7(2)	C35-O21-Co2	124.4(6)
O13-Co1-O5	93.8(2)	C1-N1-Co2	120.9(6)
O13-Co1-O9	174.0(3)	C5-N1-Co2	118.1(6)
O13-Co1-O17	90.1(3)	C5-N1-C1	121.0(7)
O15-Co1-O1	95.7(2)	C8-N2-Co3	120.6(6)
O15-Co1-O5	175.0(3)	C8-N2-C12	120.7(8)
O15-Co1-O9	90.2(3)	C12-N2-Co3	118.6(7)
O15-Co1-O13	88.2(3)	C15-N3-Co4	120.9(6)
O15-Co1-O17	87.6(3)	C15-N3-C19	121.5(8)
O17-Co1-O1	174.5(3)	C19-N3-Co4	117.2(6)
O17-Co1-O5	87.8(3)	C35-N4-C36	123.3(9)
O17-Co1-O9	95.6(3)	C35-N4-C37	120.7(10)
O3-Co2-O1	149.7(2)	C36-N4-C37	115.9(11)
O3-Co2-O6	95.3(3)	N1-C1-C2	120.6(8)
O3-Co2-O21	90.8(2)	N1-C1-C6	114.6(7)
O6-Co2-O1	84.7(2)	C2-C1-C6	124.8(8)
O6-Co2-O21	173.9(3)	C1-C2-C3	118.4(9)
O14-Co2-O1	112.5(2)	C2-C3-C4	120.2(9)
O14-Co2-O3	97.8(2)	C5-C4-C3	118.1(9)
O14-Co2-O6	88.4(3)	N1-C5-C4	121.3(8)
O14-Co2-O21	90.3(2)	N1-C5-C7	113.0(7)
O14-Co2-N1	173.1(3)	C4-C5-C7	125.7(8)
O21-Co2-O1	90.3(2)	O1-C6-C1	114.6(7)
N1-Co2-O1	73.5(2)	O2-C6-O1	127.7(8)
N1-Co2-O3	76.2(3)	O2-C6-C1	117.7(7)
N1-Co2-O6	88.9(3)	O3-C7-C5	113.8(7)
N1-Co2-O21	93.1(3)	O4-C7-O3	128.3(9)
O7-Co3-O5	149.3(3)	O4-C7-C5	117.7(8)
O10-Co3-O5	86.8(3)	N2-C8-C9	120.9(9)
O10-Co3-O7	90.0(3)	N2-C8-C13	114.4(8)
O18-Co3-O5	113.2(3)	C9-C8-C13	124.6(9)
O18-Co3-O7	97.3(3)	C10-C9-C8	118.5(10)
O18-Co3-O10	90.0(4)	C11-C10-C9	120.5(10)
O18-Co3-O19	90.6(4)	C10-C11-C12	119.7(10)
O18-Co3-N2	172.5(3)	N2-C12-C11	119.6(10)
O19-Co3-O5	92.4(3)	N2-C12-C14	114.2(9)

O19-Co3-O7	90.6(4)	C11-C12-C14	126.1(9)
O19-Co3-O10	179.1(4)	O5-C13-C8	113.8(8)
N2-Co3-O5	74.2(3)	O6-C13-O5	128.8(8)
N2-Co3-O7	75.4(3)	O6-C13-C8	117.4(8)
N2-Co3-O10	91.4(3)	O7-C14-C12	115.3(9)
N2-Co3-O19	88.2(4)	O8-C14-O7	126.5(11)
O2-Co4-O9	88.5(3)	O8-C14-C12	118.2(11)
O2-Co4-O11	89.9(3)	N3-C15-C16	121.3(9)
O2-Co4-O20	171.8(10)	N3-C15-C20	113.3(7)
O2-Co4-O20A	172.6(10)	C16-C15-C20	125.2(9)
O11-Co4-O9	150.8(2)	C15-C16-C17	118.3(10)
O11-Co4-O20	85.3(9)	C16-C17-C18	120.1(8)
O11-Co4-O20A	96.5(8)	C19-C18-C17	116.5(9)
O16-Co4-O2	90.1(3)	N3-C19-C18	122.2(9)
O16-Co4-O9	108.7(3)	N3-C19-C21	114.5(7)
O16-Co4-O11	100.4(3)	C18-C19-C21	123.3(9)
O16-Co4-O20	84.2(7)	O9-C20-C15	116.5(8)
O16-Co4-O20A	92.4(6)	O10-C20-O9	126.1(8)
O16-Co4-N3	174.0(3)	O10-C20-C15	117.4(8)
O20-Co4-O9	98.9(10)	O11-C21-C19	113.4(8)
O20A-Co4-O9	84.1(10)	O12-C21-O11	127.4(9)
N3-Co4-O2	95.2(3)	O12-C21-C19	119.2(8)
N3-Co4-O9	74.3(3)	C23-C22-C28	116.1(7)
N3-Co4-O11	76.8(3)	C27-C22-C23	121.5(8)
N3-Co4-O20	90.2(7)	C27-C22-C28	122.4(8)
N3-Co4-O20A	82.7(6)	C24-C23-C22	117.8(8)
O7-Co5-O71	119.1(6)	C23-C24-C29	118.8(8)
O221-Co5-O71	107.3(5)	C25-C24-C23	118.5(8)
O221-Co5-O7	115.9(5)	C25-C24-C29	122.7(7)
O22-Co5-O7	107.3(5)	C26-C25-C24	122.4(8)
O22-Co5-O71	115.9(5)	C25-C26-C27	119.8(8)
O22[1]-Co5-O22	87.3(10)	C22-C27-C26	119.9(8)
Co1-O1-Co2	104.3(3)	O13-C28-O14	123.2(7)
C6-O1-Co1	136.0(5)	O13-C28-C22	121.0(7)
C6-O1-Co2	116.3(5)	O14-C28-C22	115.8(7)
C6-O2-Co4	128.5(6)	O15[2]-C29-O16[2]	126.4(8)
C7-O3-Co2	118.6(6)	O15[2]-C29-C24	117.5(8)
Co1-O5-Co3	105.6(3)	O16[2]-C29-C24	116.0(8)
C13-O5-Co1	133.0(6)	C31-C30-C33	119.7(15)
C13-O5-Co3	116.9(5)	C31-C30-C34	121.8(14)
C13-O6-Co2	126.2(6)	C33-C30-C34	117.1(14)

Co5-O7-Co3	143.1(4)	C30[2]-C31-C30	122(2)
C14-O7-Co3	116.3(7)	C33-C32-C33[2]	120(2)
C14-O7-Co5	100.1(7)	C32-C33-C30	118.9(16)
Co1-O9-Co4	107.0(3)	O17-C34-C30	116.3(10)
C20-O9-Co1	136.2(6)	O18-C34-O17	127.1(10)
C20-O9-Co4	114.4(6)	O18-C34-C30	116.1(11)
C20-O10-Co3	130.2(6)	O21-C35-N4	122.2(9)
C21-O11-Co4	117.8(6)	C38-N5-C39	123(2)
C28-O13-Co1	132.9(6)	C38-N5-C40	124(3)
C28-O14-Co2	113.9(5)	C40-N5-C39	112(2)
C29[2]-O15-Co1	136.3(6)	O23-C38-N5	122(3)

[1]1-Y+X,2-Y,2/3-Z; [2]+Y,+X,-Z

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] "A" show the atoms from disordered coordinated water molecule.

Table S6. The calculated values through the bond valence sum analysis[56]

Cobalt atoms in Complex **1**	bond valence sum	Cobalt atoms in Complex **2**	bond valence sum
Co1	2.02	Co1	2.00
Co2	1.97	Co2	2.00
Co3	2.06	Co3	2.06
Co4	2.02	Co4	2.07
		Co5	1.44

Figure S1. ORTEP drawing of **1** with 30% probability thermal ellipsoids.

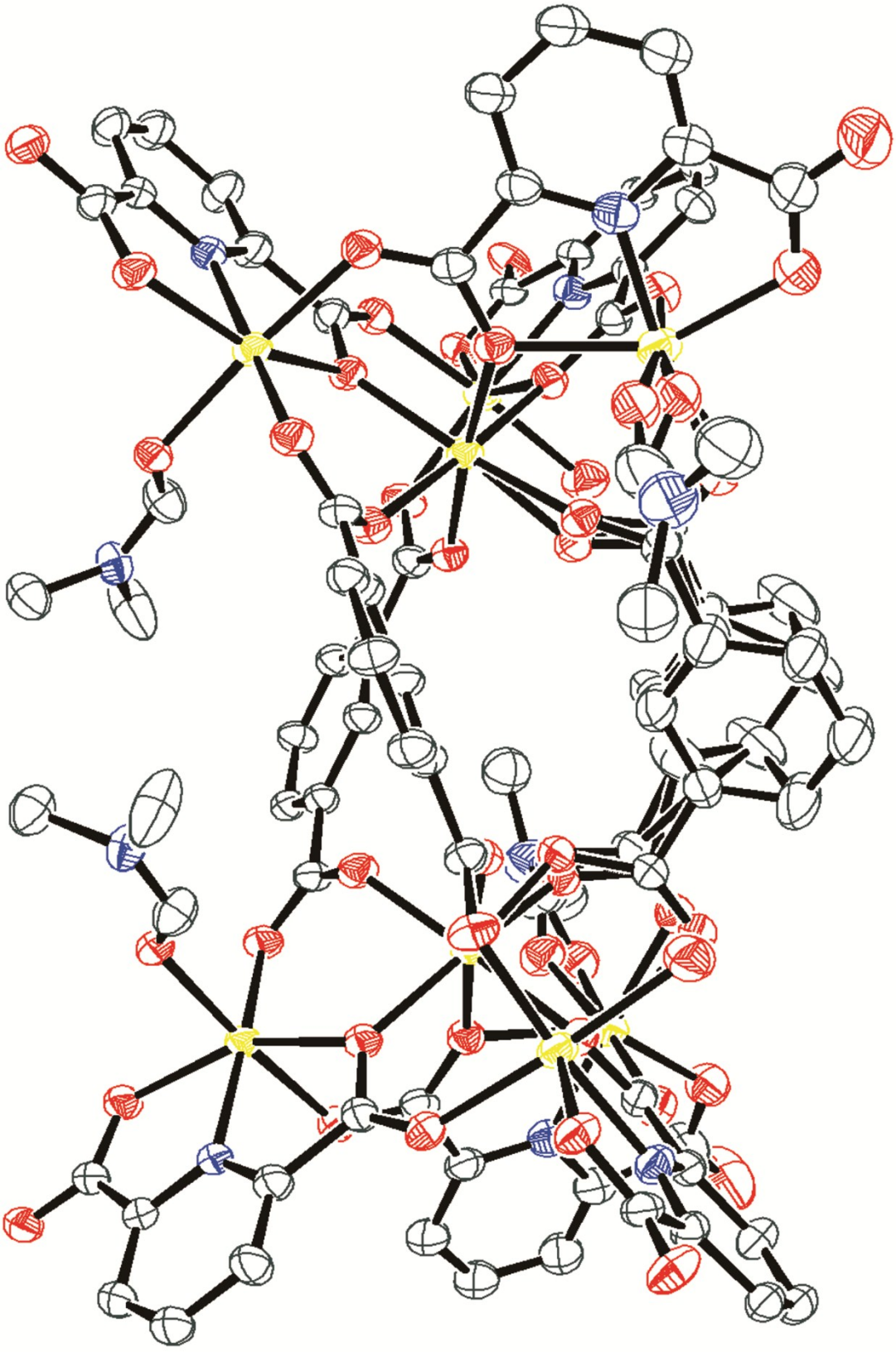


Figure S2. ORTEP drawing of **2** with 30% probability thermal ellipsoids.

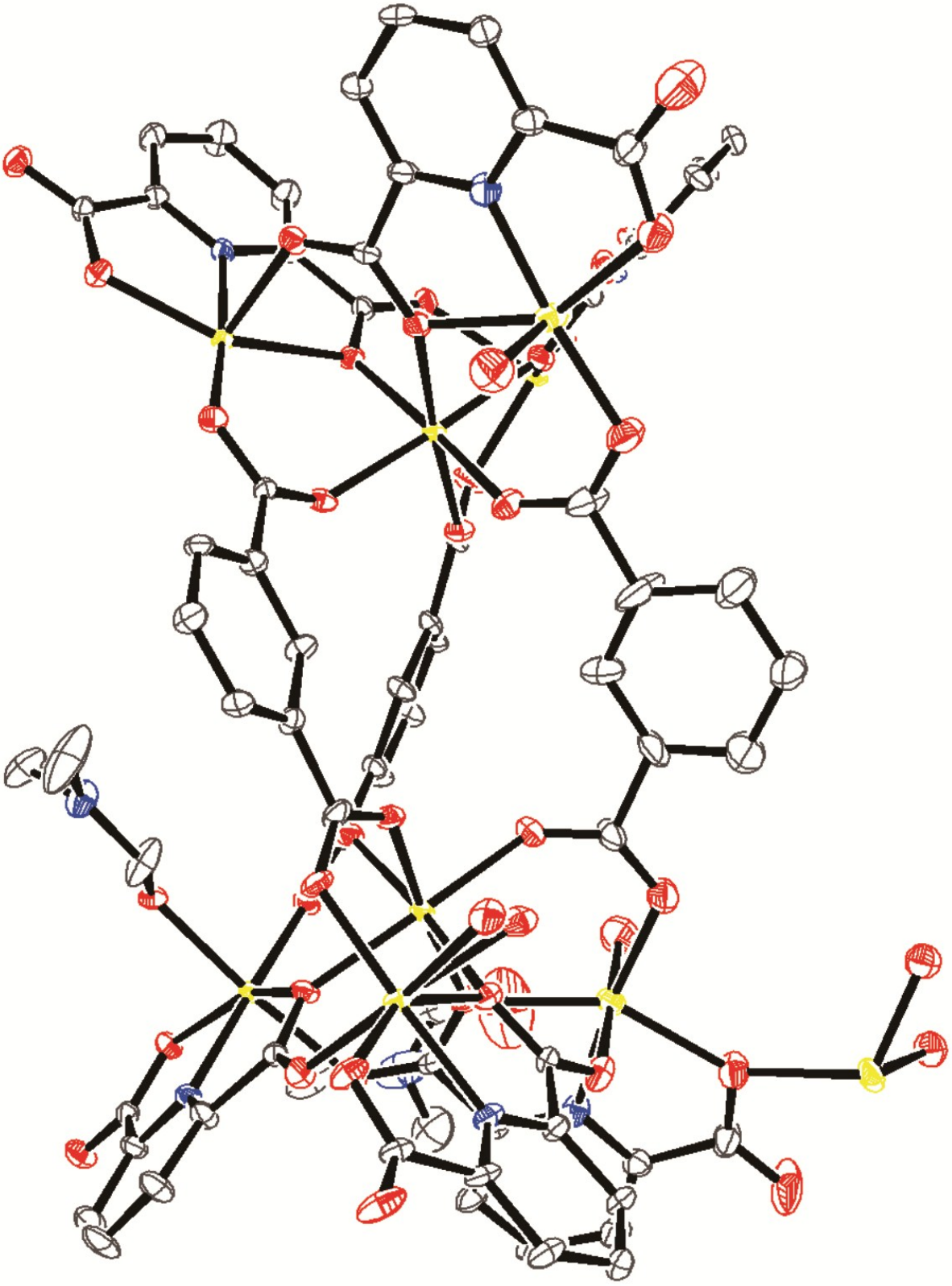


Figure S3. Thermogravimetric analysis (TGA) for $Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4$, **1**.

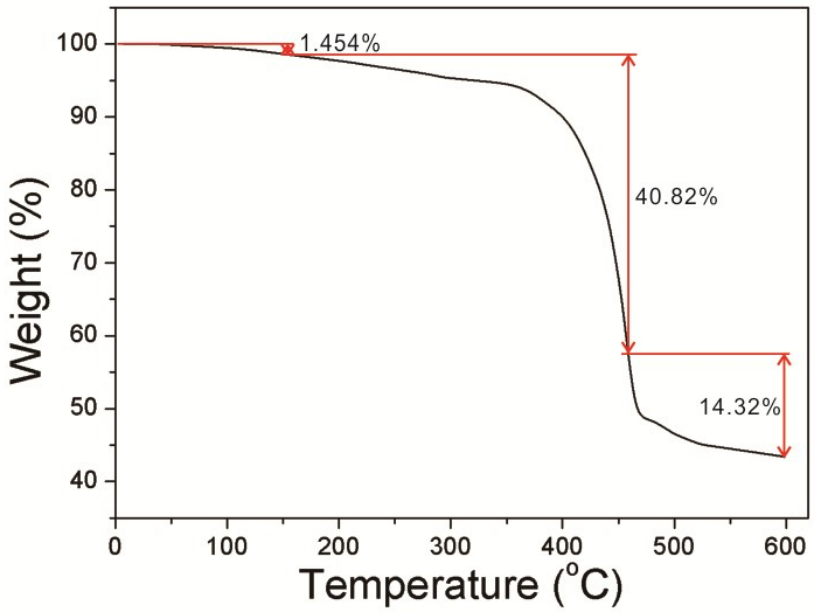


Figure S4. Thermogravimetric analysis (TGA) for $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–0.51(Co(OH_n)_2)]$, **2**

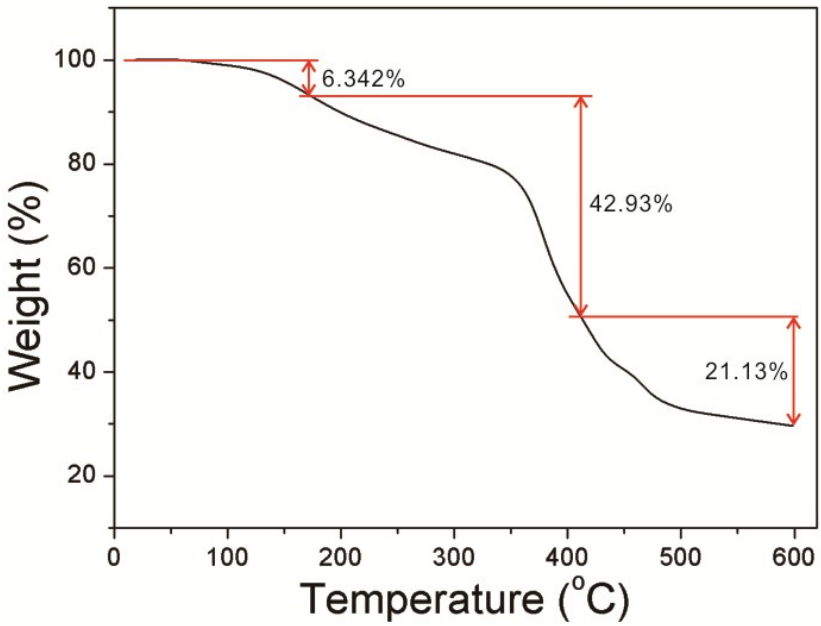


Figure S5. FT-IR spectrum for $Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4$, **1**.

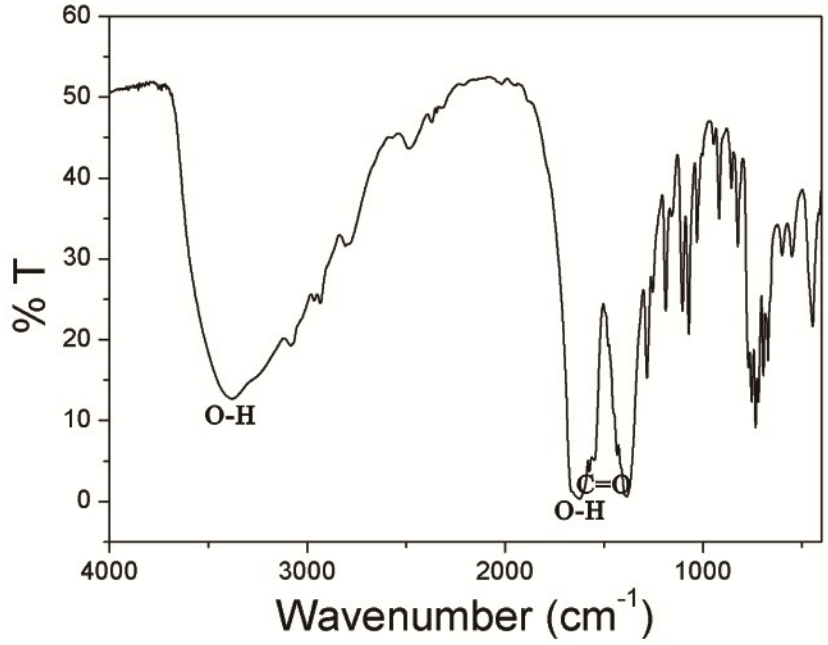


Figure S6. FT-IR spectrum for $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–0.51(Co(OH_n)_2)]$, **2**.

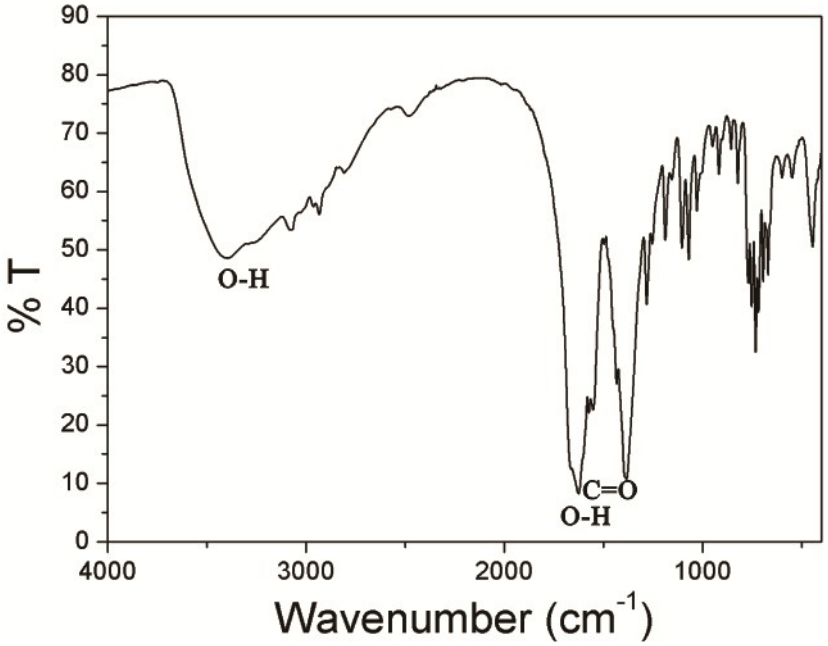


Figure S7. PXRD pattern for $Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4$, **1**: simulated (a) and experimental (b).

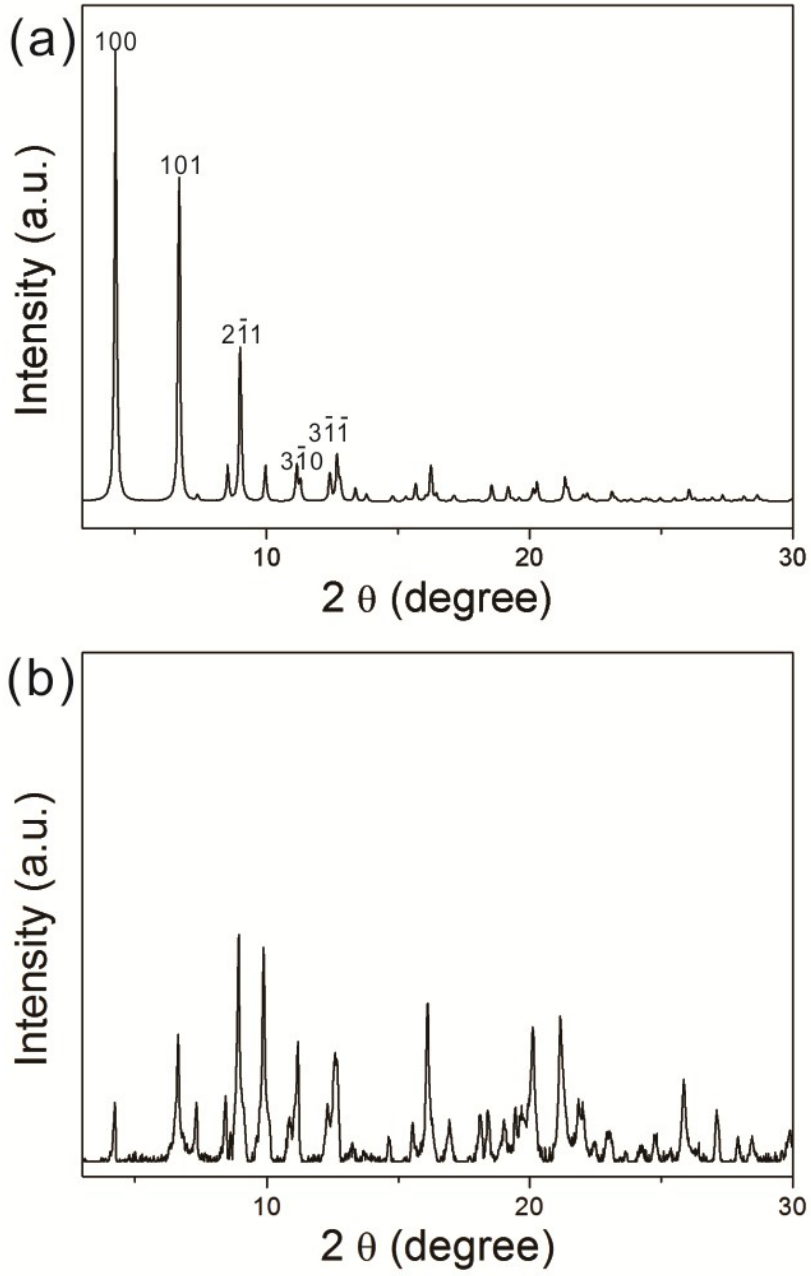


Figure S8. PXRD pattern for $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–0.51(Co(OH_n)_2)]$, **2**: simulated (a) and experimental (b).

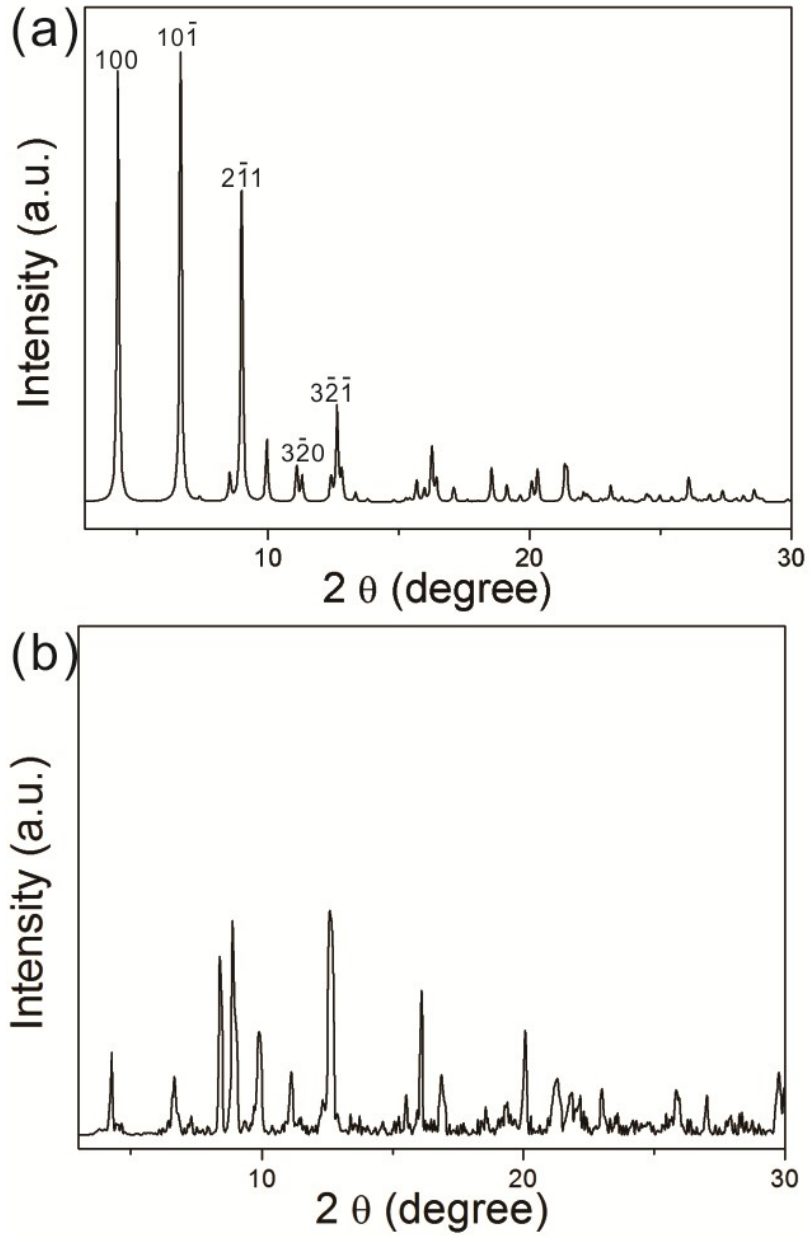
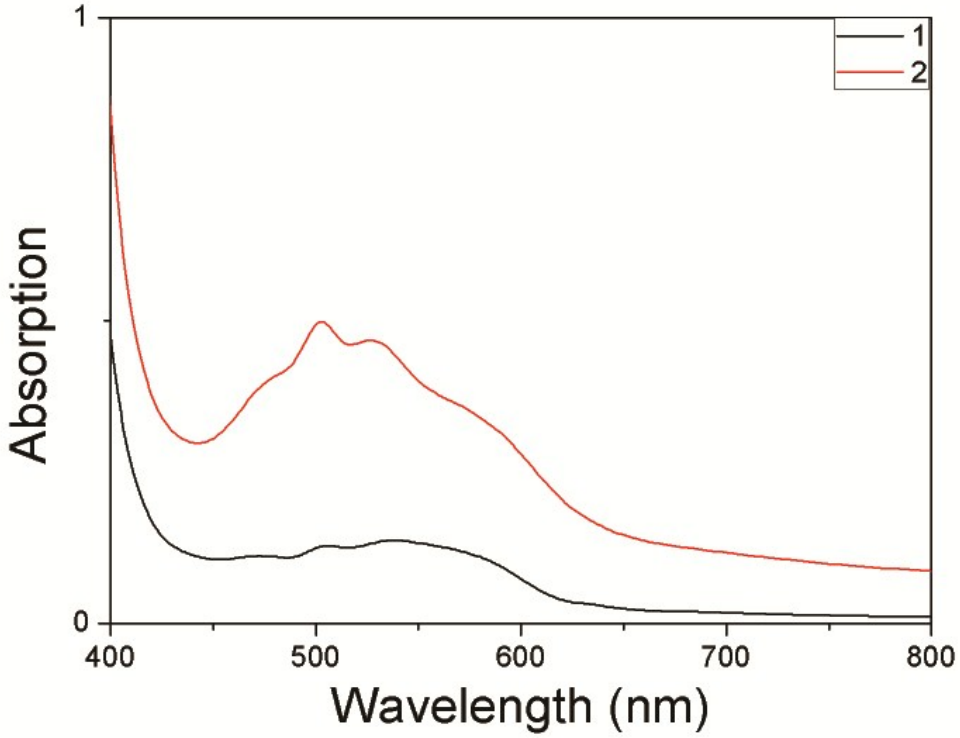


Figure S9. UV-Vis spectra of **1** and **2**



Supporting Information References:

[1] *APEX2 (version 2012.2-0)*, Data collection software, Bruker AXS Inc., Madison, Wiskonsin, (2011).
[2] *SAINT (version 6.0)*, Data integration software, Bruker AXS Inc., Madison, Wiskonsin, (2011).
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