Electronic Supporting Information (ESI)

$[Co(H_2O)_6]^{2+}$ and H_3O^+ encapsulated in a unique 3D anionic Co(II)-framework with hydrophilic hexagonal and circular channels

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Materials and Measurements: All reagents were purchased from commercial sources and used as received. Infrared spectra were obtained in KBr pellets on a Nicolet Avatar 360 FTIR spectrometer in the range of 400−4000 cm^{-1}. Elemental analyses of C, H and N were determined with a Perkin-Elmer 2400C Elemental Analyzer. Thermogravimetric analyses (TGA) were carried out in nitrogen stream using a Seiko Extar 6000 TG/DTA equipment with heating rate of 5°Cmin^{-1}. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα radiation, λ = 1.5406 Å). Magnetism measurements were performed on a Quantum Design MPMSSQUID magnetometer.

$[Co(H_2O)_6(H_3O)]\cdot3[Co_2(L)(H_2O)_2]\cdot0.5H_2O(1)$: A mixture of $Co(ClO_4)_2\cdot6H_2O$ (0.1 mmol, 36.5mg), H_5L (0.05 mmol, 18.7 mg), NaOH (0.1 mmol, 4.0 mg), and $H_2O/EtOH$ (8 mL, v:v= 1:1) was placed in a 25mL Teflon-lined stainless steel vessel, heated to 140 ° C for 3 days, and then cooled to room temperature over 24 h. Purple rod-like crystals of **1** were obtained. Yield: 16.22 mg (62% based on Co). Elemental analysis (%): calcd for $(C_{51}H_{43}Co_7O_{43.5})$: C 34.72, H 2.46; Found: C 34.79, H 2.94. IR (cm^{-1}): 3493s, 1626s, 1561s, 1442w, 1409w, 1369vs, 1205w, 1117w, 776w, 723m, 555w, 478w.

X-Ray Crystallography: Single-crystal X-ray diffraction analysis of **1** were collected on a Rigaku XtaLAB mini diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). The collected data were reduced using the program *CrystalClear*[1] and an empirical absorption

correction was applied. The structure was solved by direct methods and refined based on F^2 by the full matrix least-squares methods using SHELXTL.[2,3] All non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms bonded to the carbon atoms were included in calculated positions and allowed for with isotropic thermal parameters riding on those of the parent atoms. The crystal data and structure refinements for **1** and the selected bond distances and angles are listed in Table S1 and Table S2.

References

1   Rigaku. CrystalClear version 2.0, Rigaku Corporation, Tokyo, Japan, 2009.

2   G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.

3   G. M. Sheldrick, SHELXL, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
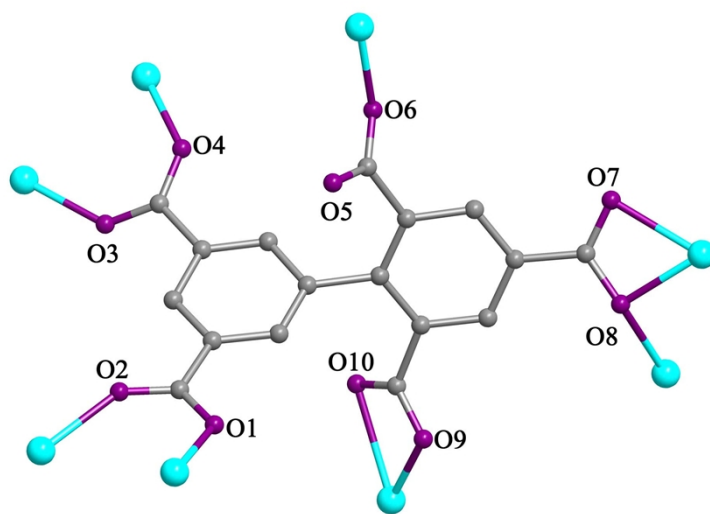
Fig. S1 The coordination modes of L^{5-} ligand in **1**.

Fig. S2 PXRD patterns of the simulated and as-synthesized samples of **1**.

Fig.S3 X-Ray photoelectron spectrum of **1**

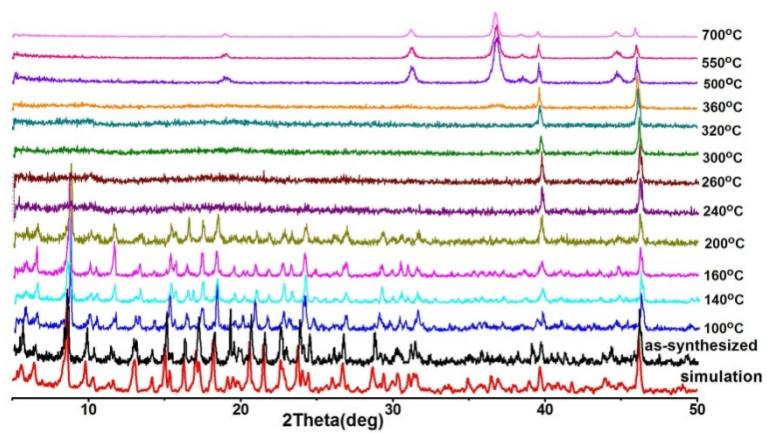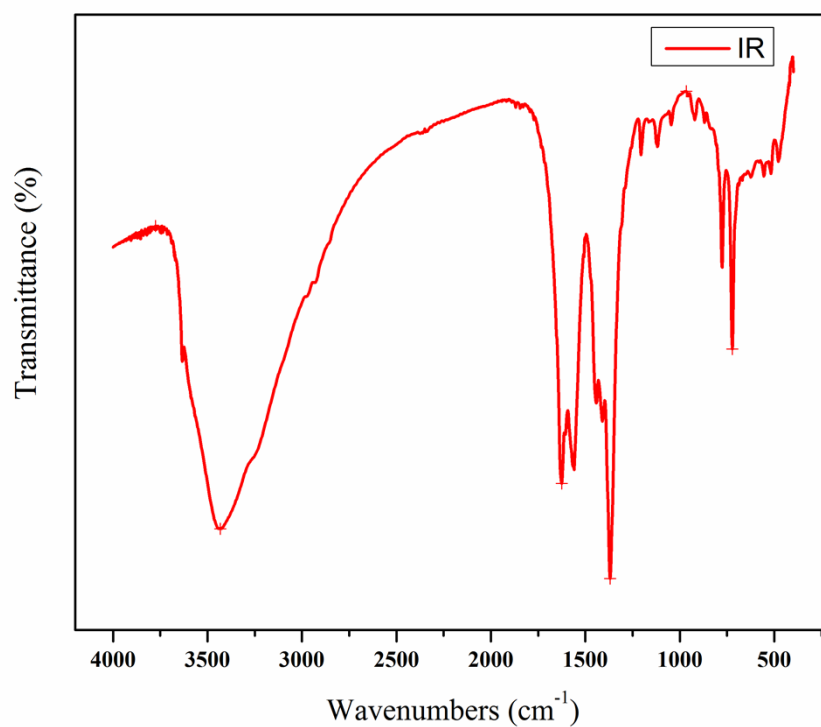**Fig.S4** TGA plot of **1**under N$_2$ atmosphere.

Fig. S5 The variable-temperature PXRD patterns of **1**.

Fig. S6 The IR spectra of **1**.

Table S1 Crystal Data and Structure Refinements for **1**

complex	**1**
Empirical formula	$C_{51}H_{43}Co_7O_{43.5}$
Formula weight	1764.36
Temperature	296(2) K
Wavelength (Å)	0.71073
Crystal system, space group	Trigonal, P31c
Z	2
a (Å)	16.2712(4)
b (Å)	16.2712(4)
c (Å)	17.2772(8)
α (°)	90
β (°)	90

γ (°)	120
Calculated density (mg m^{-3})	1.479
Absorption coefficient (mm^{-1})	1.520
$F(000)$	1772
Crystal size (mm)	0.19 x 0.18x 0.16
θ range for data collection (°)	1.86-25.05
Index range	-19<=h<=19
	-19<=k<=19
	-20<=l<=20
Reflections collected	33657
Reflections unique	4681 ($R_{(int)}$ = 0.0413)
Completeness to θ = 25.01	99.9 %
Data/restraints/parameters	4681 / 1 / 307
Goodness-of-fit on F^2	1.066
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0534, wR_2 = 0.1566
R indices (all data)	R_1 = 0.0538, wR_2 = 0.1572
Flack parameter	0.02(2)
Largest diff peak and hole (e Å^{-3})	1.762 and -0.700

[a]$R= \Sigma||F_0|-|F_C||/\Sigma|F_0|$; [b]$wR_2 = [\Sigma[w(F_0{}^2-F_C{}^2)^2]/\Sigma[(F_0{}^2)^2]]^{1/2}$

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

			1
Co(1)-O(4)#1	1.991(4)	Co(2)-O(11)	2.133(5)
Co(1)-O(9)#2	2.012(4)	Co(2)-O(8)#3	2.196(4)
Co(1)-O(1)	2.021(4)	Co(3)-O(13)#5	2.081(5)
Co(1)-O(8)#3	2.098(4)	Co(3)-O(13)	2.081(5)
Co(1)-O(7)#3	2.263(5)	Co(3)-O(13)#2	2.081(5)
Co(2)-O(6)#4	2.036(4)	Co(3)-O(14)#5	2.089(6)
Co(2)-O(3)#1	2.036(4)	Co(3)-O(14)#2	2.089(6)
Co(2)-O(2)	2.098(4)	Co(3)-O(14)	2.089(6)
Co(2)-O(12)	2.125(5)		

O(4)#1-Co(1)-O(9)#2	98.0(2)	O(6)#4-Co(2)-O(12)	93.1(2)
O(4)#1-Co(1)-O(1)	104.4(2)	O(3)#1-Co(2)-O(12)	87.8(2)
O(9)#2-Co(1)-O(1)	96.59(19)	O(2)-Co(2)-O(12)	172.5(2)
O(4)#1-Co(1)-O(8)#3	99.1(2)	O(6)#4-Co(2)-O(11)	94.63(19)
O(9)#2-Co(1)-O(8)#3	145.56(18)	O(3)#1-Co(2)-O(11)	88.97(19)
O(1)-Co(1)-O(8)#3	107.70(17)	O(2)-Co(2)-O(11)	85.14(19)
O(4)#1-Co(1)-O(7)#3	155.6(2)	O(12)-Co(2)-O(11)	87.5(2)
O(9)#2-Co(1)-O(7)#3	95.75(18)	O(6)#4-Co(2)-O(8)#3	87.24(18)
O(1)-Co(1)-O(7)#3	93.8(2)	O(3)#1-Co(2)-O(8)#3	89.20(18)
O(8)#3-Co(1)-O(7)#3	59.39(16)	O(2)-Co(2)-O(8)#3	97.52(17)
O(6)#4-Co(2)-O(3)#1	176.3(2)	O(12)-Co(2)-O(8)#3	89.8(2)
O(6)#4-Co(2)-O(2)	88.8(2)	O(11)-Co(2)-O(8)#3	176.79(18)
O(3)#1-Co(2)-O(2)	90.7(2)	O(13)-Co(3)-O(14)#2	178.7(2)
O(13)#5-Co(3)-O(13)	89.0(2)	O(13)#2-Co(3)-O(14)#2	89.7(2)
O(13)#5-Co(3)-O(13)#2	89.0(2)	O(14)#5-Co(3)-O(14)#2	90.9(2)
O(13)-Co(3)-O(13)#2	89.0(2)	O(13)#5-Co(3)-O(14)	178.7(2)
O(13)#5-Co(3)-O(14)#5	90.9(2)	O(13)-Co(3)-O(14)	90.9(2)
O(13)-Co(3)-O(14)#5	89.7(2)	O(13)#2-Co(3)-O(14)	89.7(2)
O(13)#2-Co(3)-O(14)#5	178.7(2)	O(14)#5-Co(3)-O(14)	90.4(3)
O(13)#5-Co(3)-O(14)#2	89.7(2)	O(14)#2-Co(3)-O(14)	90.4(3)

Symmetry codes: #1: -y+2, x-y+1, z; #2: -x+y+1, -x+1, z; #3: x-y+1, -y+1, z+1/2; #4: y, x, z+1/2; #5: -y+1, x-y, z

Table S3. Coordination number (*N*), bond valence sum (*BVS*), expected atomic valence (*V*) and deviation from the expected atomic valence (Δ*V*) for the cobalt cations.

	P5		
	Co1	Co 2	Co3
N	5	6	6
BVS	1.93	1.94	2.08
V	+2	+2	+2
Δ*V*	0.07	0.06	0.08

The atomic valences for six cobalt cations can be determined by the bond valence model . According to this model, the sum of all the bond valences around any ion is equal to its ionic charge or valence. Here, bond valences (s) are calculated as $s = \exp[(r_0 - r)/B]$; B=0.37, r_0=1.692 for Co(II)-O pairs, r_0=1.70 for Co(III)-O pairs . The calculated results are listed in Table X. Evidently, the calculated values of bond valence sum are in good agreement with the values of expected atomic valence, which indicates that all the cobalt cations have a valence of **1**.