Supporting Information

for

A Unique 2D→3D Polycatenation Cobalt(II)-Based Molecule Magnet Showing Coexistence of Paramagnetism and Canted Antiferromagnetism †

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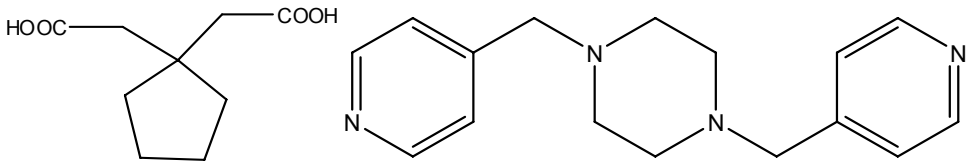
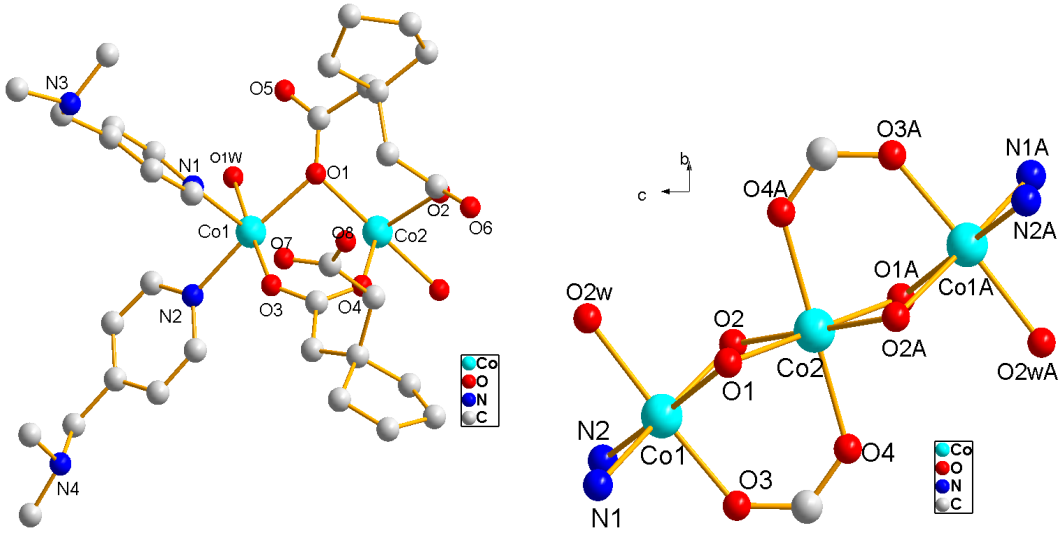
Experiment Section

Materials and general methods: A piperazine-pyridine ligand, 1,4-bis (pyridin-4-ylmethyl)piperazine (bpmp), was prepared according to a previously reported procedure.[1] All commercially available reagents and starting materials were of reagent-grade quality and used without further purification. Elemental analyses (C, H, N) were carried out on an Elementar Vario EL III analyzer. Infrared (IR) spectra were recorded on PerkinElmer Spectrum One as KBr pellets in the range 4000-400 cm^{-1}. Thermogravimetric analysis was recorded with a NETZSCH STA 449C unit at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. X-ray Powered diffraction (XRPD) patterns of the samples were recorded by an X-ray diffractometer (MiniFlex2 goniometer).

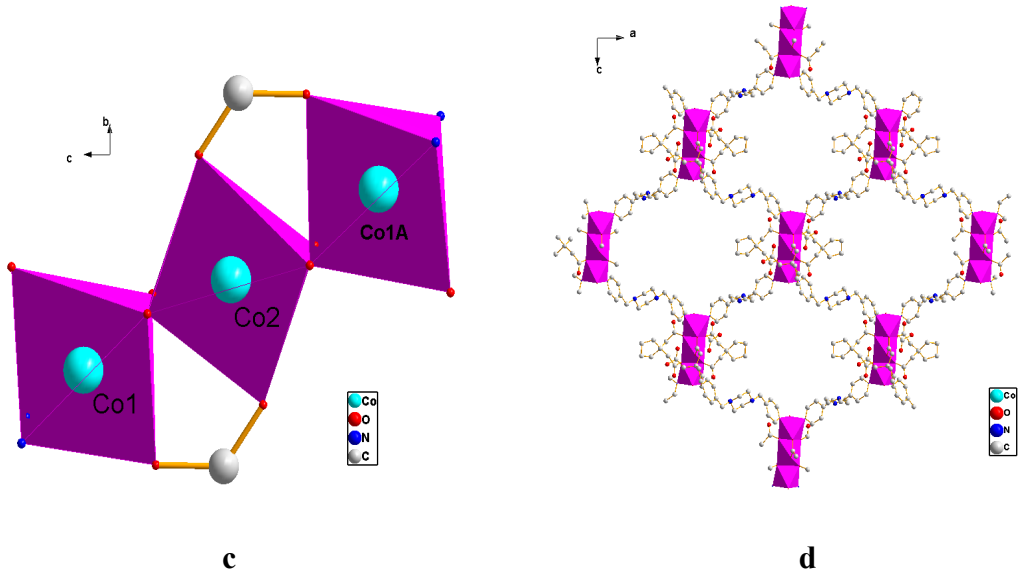
Synthesis of $[Co_{1.5}(bpmp)(Hcda)(cda)(H_2O)]$ (1): $Co(NO_3)_2 \cdot 6H_2O$ (0.1mmol), bpmp (0.1mmol), H_2mip (0.1mmol), and NaOH (0.2mmol) in 8ml water and stirred for 30 min in air. Then the mixture was transferred to a 25 mL stainless-steel reactor with Teflon liner and heated to 120 °C in 3 hours. The temperature was kept at 120 °C for 3 days and cooled to room temperature during 24 hours. Red cubic crystals were isolated and have been characterized by single crystal X-ray analyses. Yield: 57% (based on Co). Calcd for $C_{34}H_{47}N_4O_9Co_{1.5}$ (744.16):: C 54.88, H 6.36, N 7.53; found: C 54.91, H 6.32, N 7.55. IR (KBr, cm^{-1}): 3405 (w, br), 3068 (m), 2936 (m), 2880 (m), 2768 (m), 2545 (w), 1986 (w), 1713 (m), 1560 (s), 1408 (s), 1375 (s), 1293 (m), 1260 (m), 1229 (m), 1176 (s), 1161 (m), 1139 (m), 1647 (m), 1013 (m), 930 (w), 845 (s), 805 (m), 726 (s), 654 (m), 609 (m), 556 (m), 491 (m).



Scheme 1 Scheme of H_2dca and bpmp ligand



a **b**



c **d**

Fig. S1 (a) Basic building block in complexe **1**, showing the coordination environment around the cobalt atom; (**b**) Coordination environment of the Co_3 cluster in **1**; **(c)** Coordination polyhedron of the Co_3 cluster in **1**; (**d**) (4,4) layer in **1**.

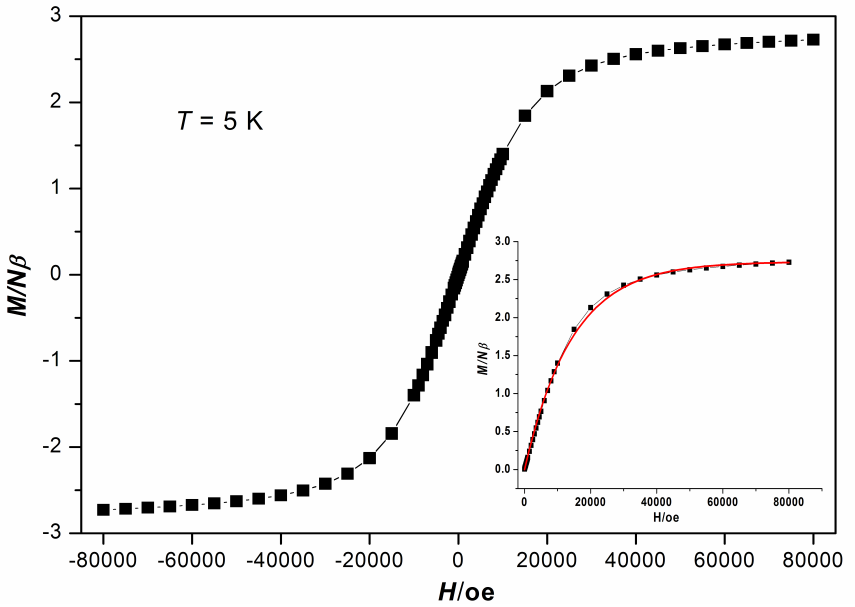


Fig. S2 Field dependence of the magnetization for **1** at 5 K. Insert: Brillouin fitting with S = 3/2 and g = 2.7 for the *M* versus *H* curve at 5 K for **1**.

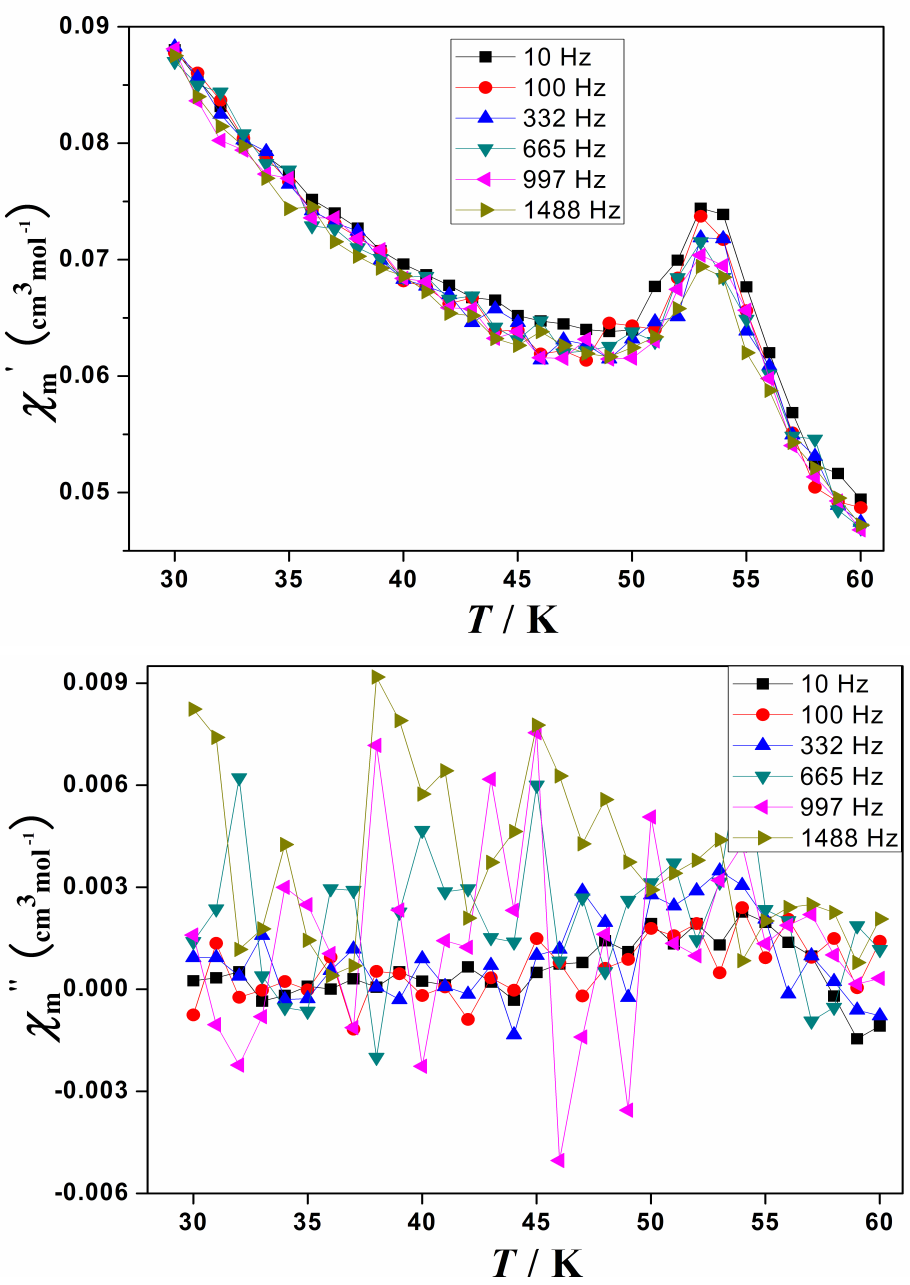


Figure S3. Temperature dependence of the in-phase (top) and out-phase (bottom) components of the ac susceptibility of **1** in zero applied DC field, along with an oscillating field of 3 Oe at a frequency of 10-1500 Hz.

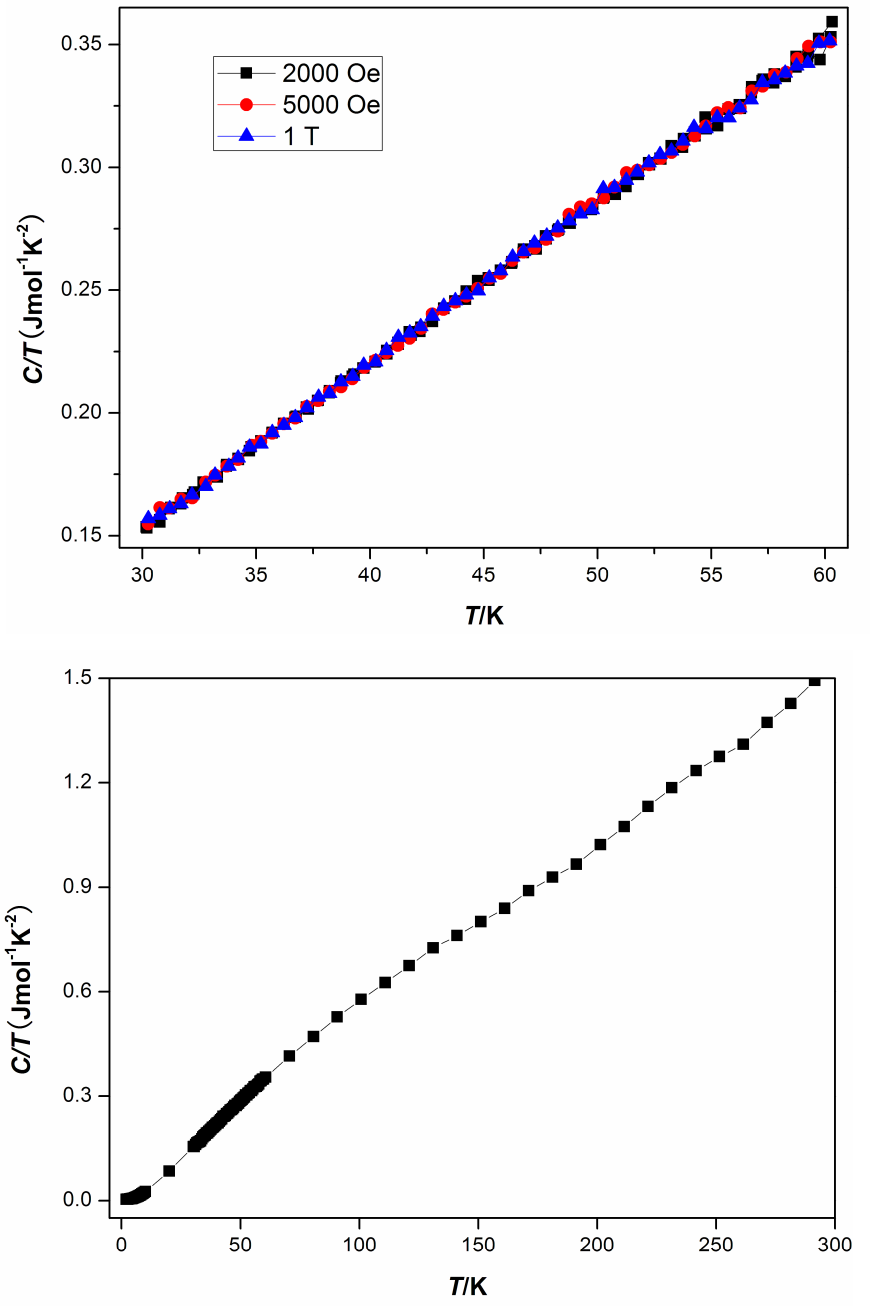


Figure S4. Top: Heat capacity measured in different magnetic fields in the temperature range of 60-2 K.

Bottom: Heat capacity measured in zero magnetic field in the temperature range of 300-2 K.

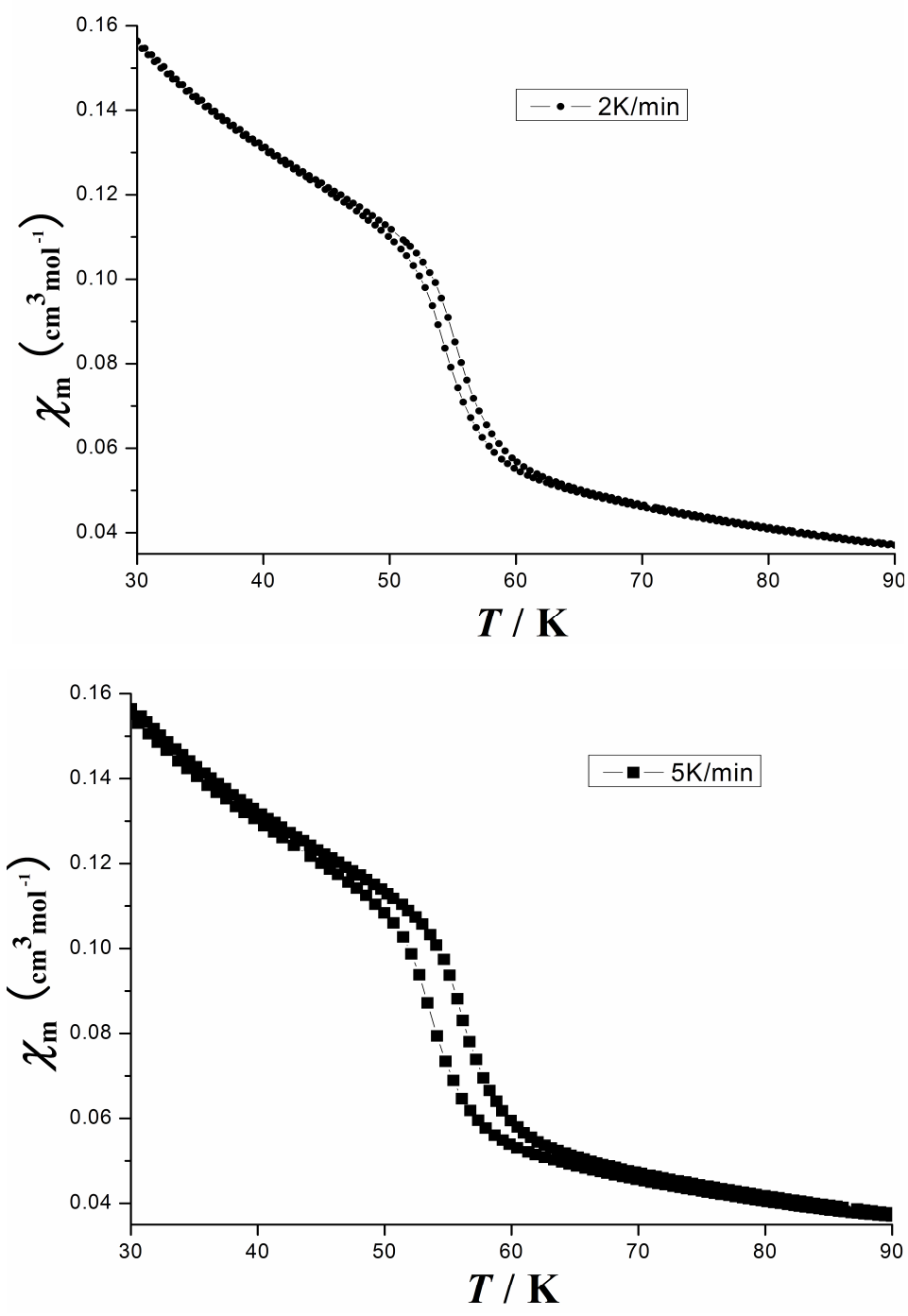


Fig. S5 Temperature dependence of the magnetic susceptibility curves in the temperature range of 90-30-90 K as the temperature vary with 2K/min or 5K/min respectively under an applied field of 1000 Oe.

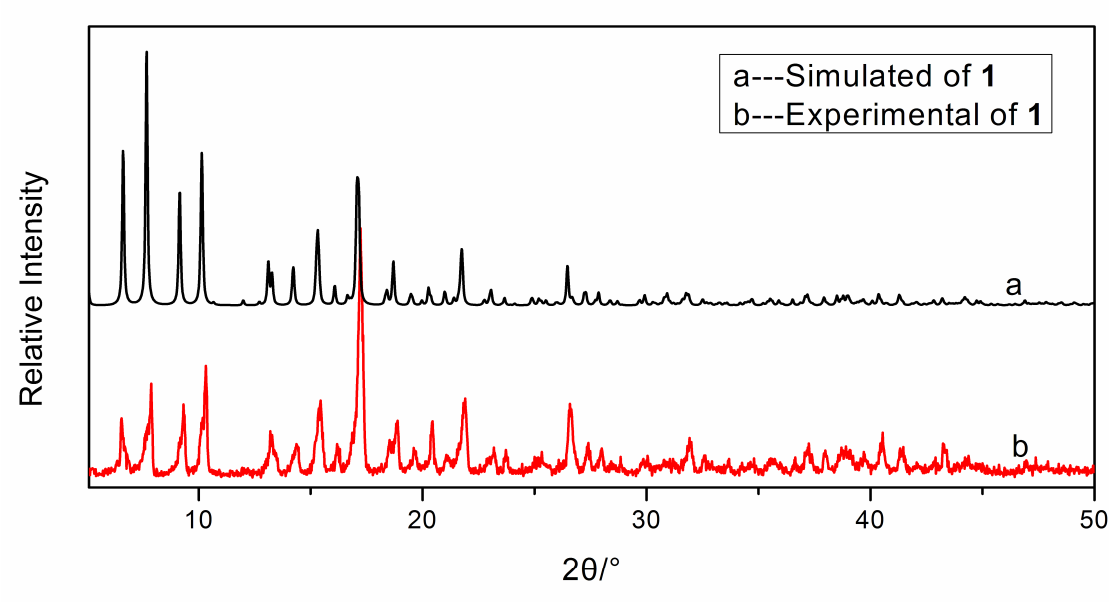


Fig. S6 X-Ray powder diffraction pattern of **1**.

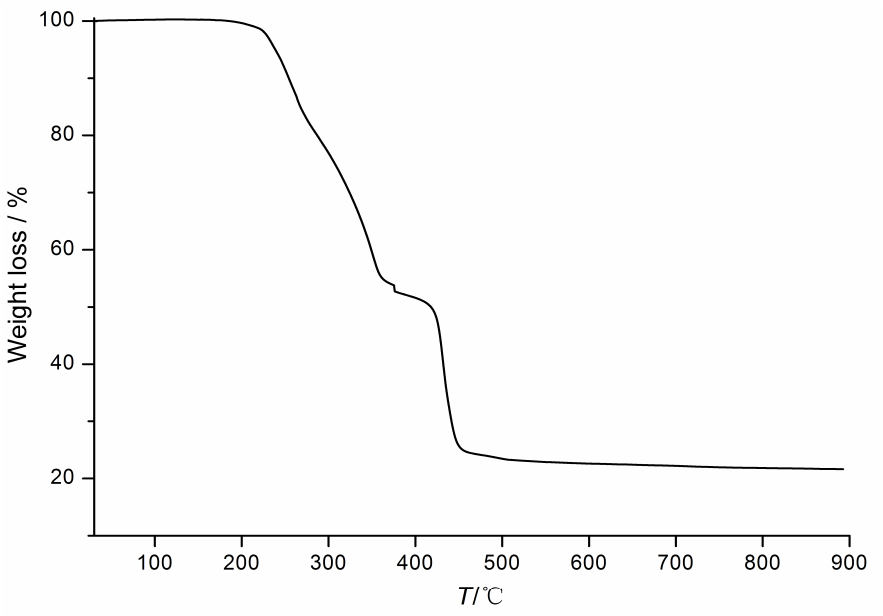


Fig. S7 TGA curve for compound **1**.

Table S1. Crystallographic data for complexe 1.

	1
Formula	$C_{68}H_{94}N_8O_{18}Co_3$
Fw	1488.30
Crystal size (mm)	0.20×0.18×0.15
Crystal system	Monoclinic
Space group	*C2/c*
a/Å	23.085(6)
b/Å	26.728(6)
c/Å	11.639(3)
β/º	90.199(6)
V/Å^3	7181(3)
Z	4
D_c/g cm^{-3}	1.377
μ/mm^{-1}	0.758
F(000)	3132
T/K	298(2)
λ(MoKα)/Å	0.71073
Reflections collected	22187
Unique reflections	8037
Parameters	446
S on F^2	1.069
R_1 (I > 2σ(I))[a]	0.0414
$_wR_2$ (I > 2σ(I))[b]	0.1053
R_1 (all data)[a]	0.0523
$_wR_2$ (all data)[b]	0.1130
$\Delta\rho_{max}$ and $_{min}$ [e/Å^3]	0.470 and -0.344

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond lengths (A°) and angles (deg) for complexe 1.

Compound **1**			
Co1-O1	2.1407(14)	Co1-O5^{i}	2.1409(14)
Co1-O3	2.0347(15)	Co1-O1W	2.1202(15)
Co1-N1	2.1440(18)	Co1-N2	2.1586(18)
Co2-O4	2.0865(14)	Co2-O1	2.0928(14)
Co2-O4^{i}	2.0865(14)	Co2-O1^{i}	2.0928(14)
Co2-O5	2.0943(13)	Co2-O5^{i}	2.0943(13)
O(3)-Co(1)-O(1W)	177.41(6)	O(3)-Co(1)-O(1)	90.41(6)
O(1W)-Co(1)-O(1)	88.75(6)	O(3)-Co(1)-O(5)^{i}	87.86(6)
O(1W)-Co(1)-O(5)^{i}	89.59(6)	O(1)-Co(1)-O(5)^{i}	80.79(5)
O(3)-Co(1)-N(1)	91.22(7)	O(1W)-Co(1)-N(1)	91.28(7)
O(1)-Co(1)-N(1)	93.42(6)	O(5)^{i} -Co(1)-N(1)	174.13(6)
O(3)-Co(1)-N(2)	89.73(7)	O(1W)-Co(1)-N(2)	90.80(7)
O(1)-Co(1)-N(2)	172.93(6)	O(5)^{i} -Co(1)-N(2)	92.15(6)
N(1)-Co(1)-N(2)	93.64(7)	O(4)-Co(2)-O(4)^{i}	180.00(2)
O(4)^{i} -Co(2)-O(1)	87.81(6)	O(4)^{i} -Co(2)-O(1)^{i}	92.19(6)
O(4)-Co(2)-O(1)	92.19(6)	O(4) -Co(2)-O(1)^{i}	87.81(6)
O(4)-Co(2)-O(5)^{i}	91.16(5)	O(1)-Co(2)-O(5)^{i}	83.01(6)
O(4)-Co(2)-O(5)	88.84(5)	O(1)-Co(2)-O(5)	96.99(6)

Symmetry code for **1**: i -x+1/2,-y+1/2,-z;

Reference

[1] Y.Y. Niu, H.W. Hou, Y.L. Wei, Y.T. Fan, Y. Zhu, C.X. Du, Inorg. Chem. Commun. 4 (2001) 358.