

# Rare double spin canting antiferromagnetic behaviours in a [Co<sub>24</sub>] cluster

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## EXPERIMENTAL SECTION

All reagents were purchased from commercial sources and used without further purification.

### Physical measurements

IR spectra were recorded as KBr pellets on a Perkin-Elmer FT-IR spectrometer in the range 4000–450 cm<sup>-1</sup>. Elemental analyses were performed with a Carlo ERBA 1106 analyzer. The variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-5 SQUID magnetometer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/Max 2500 diffractometer (CuK $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ).

### Synthesis of ligand [H<sub>2</sub>ampc]Cl

30% Me<sub>2</sub>NH aqueous solution (1 mL,  $\rho = 0.68 \text{ g} \cdot \text{mL}^{-1}$ , containing 4.53 mmol Me<sub>2</sub>NH) was added to a solution of 20 mL dry CH<sub>3</sub>CH<sub>2</sub>OH containing 4'-(bromomethyl)biphen-yl-2-carboxylic acid methyl ester (2.76g, 9.06mmol). After the mixture was refluxed for 4 h with stirring, 10% KOH aqueous solution (10 mL) was added into it and refluxed for another 1 h. And then the hydrochloric solution (1 mol·L<sup>-1</sup>, ca. 18.5mL) was added dropwise to the mixture solution with stirring until the white precipitate was deposited completely. The precipitate was filtered, washed using water and dried over phosphorus pentoxide. Yield: 1.25g (60%). Elemental analysis *calcd* (%) for C<sub>30</sub>H<sub>28</sub>NO<sub>4</sub>Cl: C 71.78, H 5.62, N 2.79; found: C 71.53, H 5.75, N 3.14; IR (KBr pellet): 3490, 3382, 2976, 2542, 1760, 1676, 1480, 1449, 1291, 1263, 857, 762 cm<sup>-1</sup>.

### Synthesis of cluster [Co<sub>24</sub>]

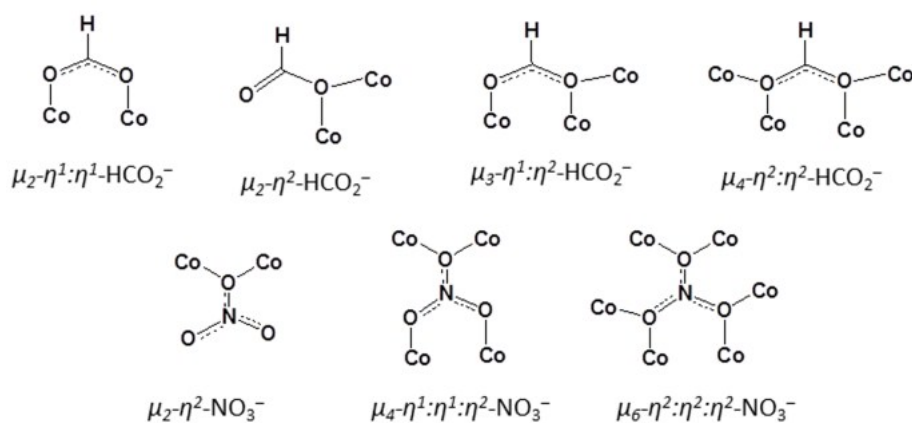
After Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0291g, 0.1mmol) was added to a solution of [H<sub>2</sub>ampc]Cl (0.0251g, 0.05mmol) in 8 ml DMF/H<sub>2</sub>O (v/v 1:1) in a 20ml vial, the vial was sealed and heated at 80°C for 10 days, and then cooled to room temperature slowly. The resulted pink block crystals were filtered, washed by CH<sub>3</sub>OH and dried under vacuum. Yield: ca. 54% based on Co<sup>2+</sup> ions. Elemental analysis *calcd* (%) for C<sub>145</sub>H<sub>161</sub>Co<sub>24</sub>N<sub>9</sub>O<sub>101</sub>·8H<sub>2</sub>O: C 33.46, H 3.43, N 2.42; found: C 33.08, H 3.82, N 2.74; IR (KBr pellet): 3432, 3059, 2927, 2866, 2385, 1707, 1584, 1554, 1448, 1387, 856, 758, 656 cm<sup>-1</sup>.

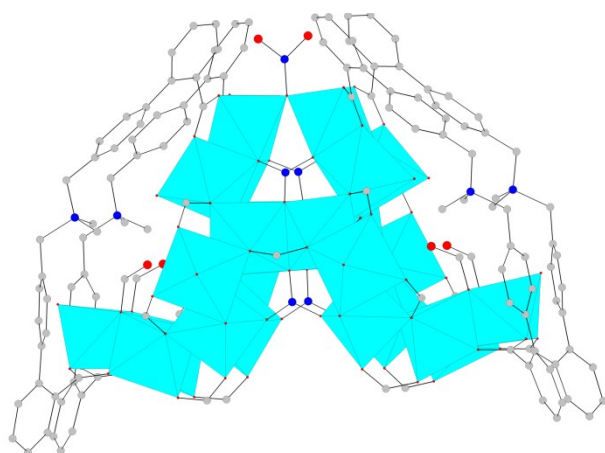
### Crystal Structure Determination

Crystal data and experimental details for **1** were given in Table S1. X-ray Diffraction data of complex **1** were obtained at 1W1A, Beijing Synchrotron Radiation Facility ( $\lambda = 0.75 \text{ \AA}$ ) at 107 K. All calculations were performed with SHELX-97 crystallographic software package. The structures were solved by the standard direct method and refined in the anisotropic approximation. Hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. For compound **1**, only methanol molecules were determined by the SHELX-97 refinement. There are a number of seriously disordered water molecules, which could not be adequately modeled. The final refinements have been carried out with SQUEEZE data.

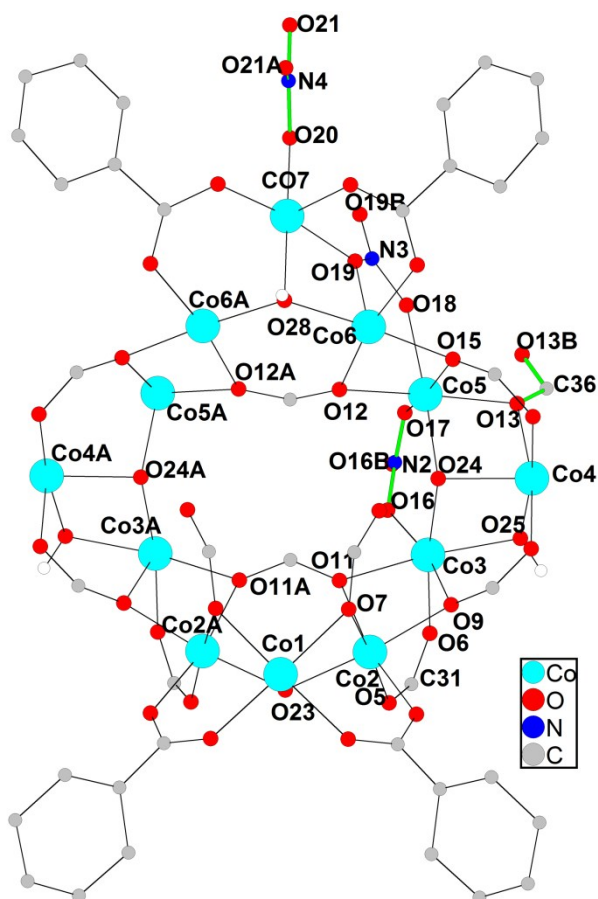
**Table S1** Crystal data and structure refinement for **1**

Empirical formula	C <sub>145</sub> H <sub>161</sub> N <sub>9</sub> O <sub>101</sub> Co <sub>24</sub>
Formula weight	5060.15
Crystal system	tetragonal
Space group	<i>P</i> -4 <i>2</i> <sub>1</sub> <i>m</i>
<i>a</i> (Å)	27.646(5)
<i>b</i> (Å)	26.0104(6)
<i>c</i> (Å)	17.306(3)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	13227(4)
<i>Z</i>	2
$\rho_{calc}$ (g/cm <sup>3</sup> )	1.271
$\mu$ (mm <sup>-1</sup> )	1.534
$\theta$ range for data collection	1.46 to 22.30
Reflections collected	26824
Independent reflections	7403
Data/restraints/parameters	7403 / 0 / 656
Goodness of fit ( GOF )	1.038
Final R indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> ) ]	0.0662
R indices ( all data )	0.0695
Largest diff. peak / hole /eÅ <sup>-3</sup>	0.884/-0.535

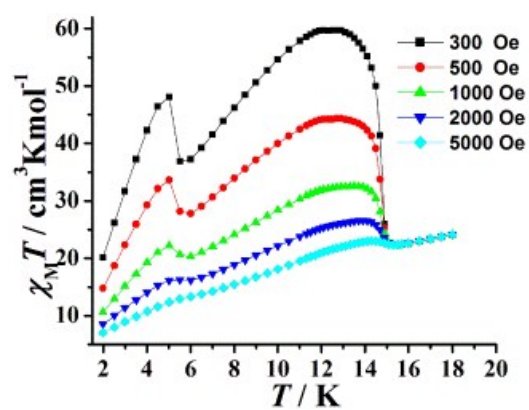
**Scheme S1.** the coordination modes of HCO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> in **1**.



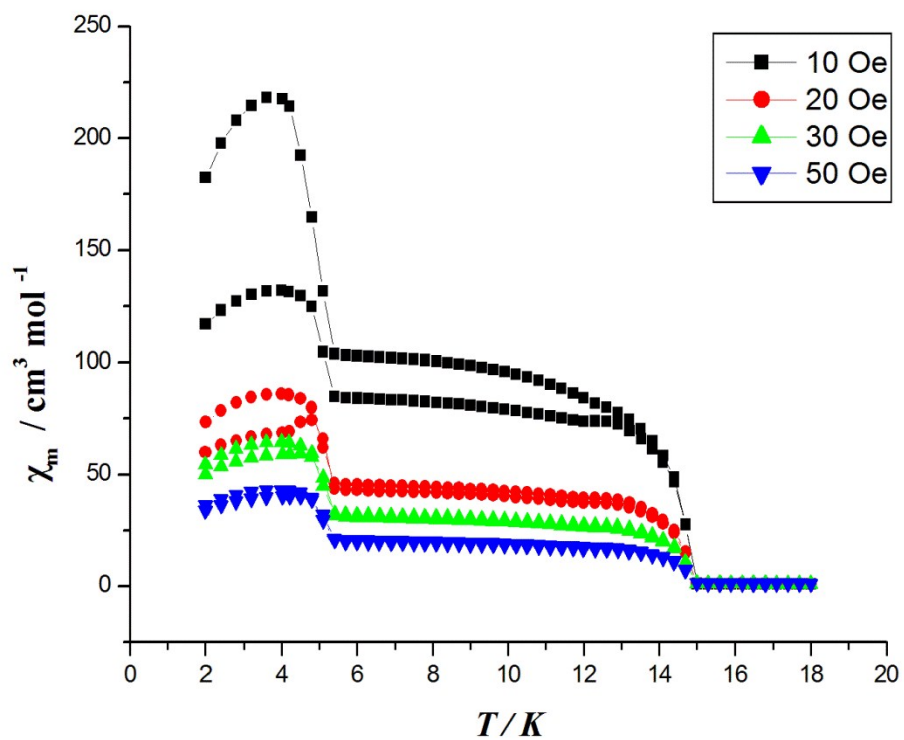
**Fig. S1.** The polyhedral structure of cluster  $[\text{Co}_{24}]$



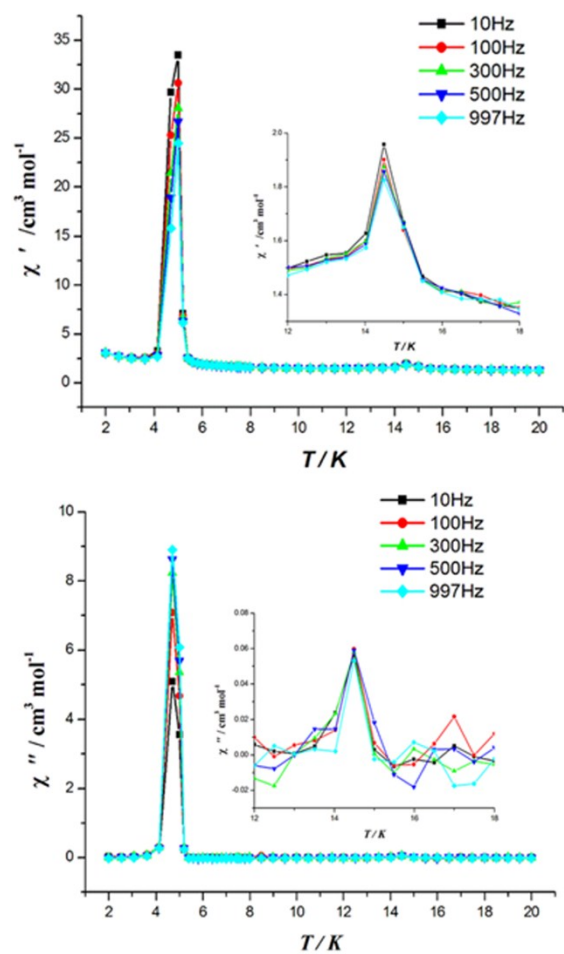
**Fig. S2.** The detail coordination environment of  $\text{Co}^{2+}$  ions in the  $[\text{Co}_3]_4$  ring, green colored bonds showing the  $\text{NO}_3^-$  and  $\text{HCO}_2^-$  groups bridging two symmetric  $[\text{Co}_3]_4$  rings: the  $\mu_2\text{-}\eta^2\text{-NO}_3^-$  group of N4/O21/O21A bridges Co7 and its symmetric atom in another  $[\text{Co}_3]_4$  rings; the  $\mu_6\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-NO}_3^-$  group of N3/O18/O19/O19B bridges three Co atoms of Co5/Co6/Co7 and their symmetric atoms in another  $[\text{Co}_3]_4$  rings; the  $\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-NO}_3^-$  group of N2/O16/O17/O16B bridges Co3/Co5 and their symmetric atoms in another  $[\text{Co}_3]_4$  rings; the  $\mu_4\text{-}\eta^2\text{:}\eta^2\text{-HCO}_2^-$  group of C36/O13/O13B bridges Co4/Co5 and their symmetric atoms in another  $[\text{Co}_3]_4$  ring. Symmetry codes: A,  $3/2-y, 3/2-x, z$ ; B,  $-1/2+y, 1/2+x, z$ .



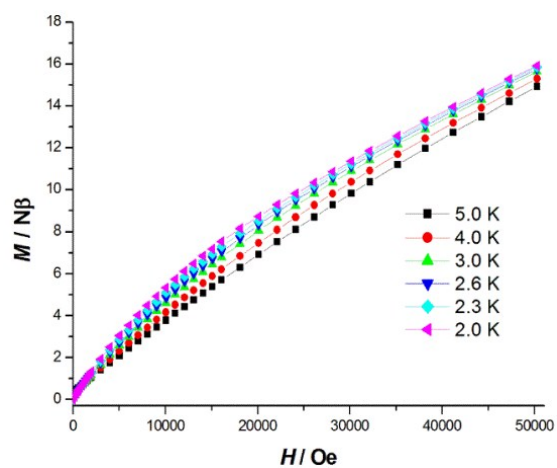
**Fig. S3.** Plots of  $\chi_M T$  data versus  $T$  at different  $dc$  fields between 2-18 K.



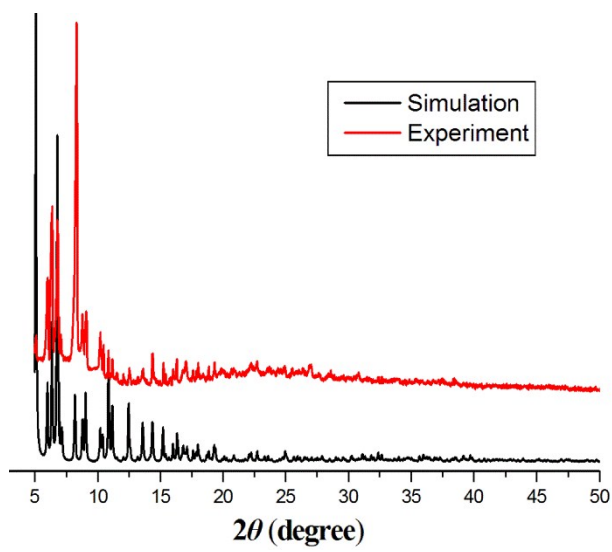
**Fig. S4.** Plots of FC and ZFC data versus  $T$  for **1** at the different magnetic fields, showing the divergence of ZFC and FC collapses together with the applied field increases.



**Fig. S5.** In-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) components for **1** with increasing frequencies Insets: the enlarging peaks of  $\chi'$  and  $\chi''$  at 14.5 K.



**Fig. S6.** Field dependence of the magnetization  $M$  between 2.0-5.0 K.



**Fig. S7** PXRD pattern of complex 1.