Magnetic relaxation in a Co(II) chain complex: synthesis, structure, and DFT computational coupling constant

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Structure description

Fig. S1. FT-IR spectra of **1** at room temperature.
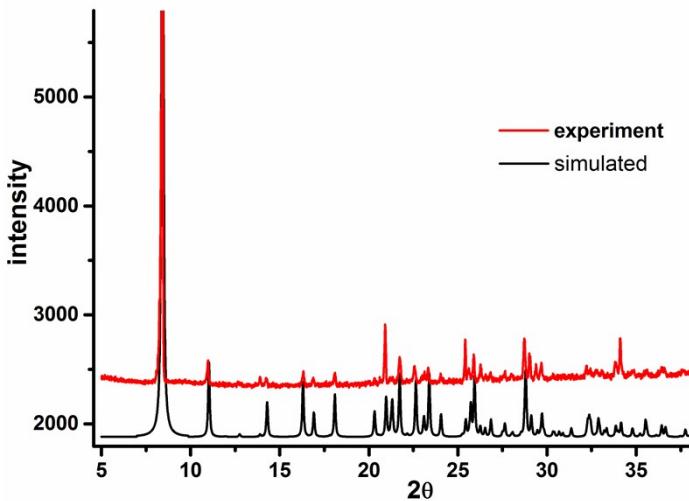
Fig. S2. XRD of **1** at room temperature.

Table S1. Hydrogen bonds for **1** [Å and °.].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(14)-H(14A)···N(6)	0.93	2.62	2.932(2)	100.5
C(18)-H(18A)···Cl(2)	0.96	2.78	3.659(2)	152.7
C(11)-H(11A)···Cl(1)[a]	0.93	2.84	3.7659(17)	177.2
C(18)-H(18B)···Cl(1)[b]	0.96	2.91	3.651(2)	134.5
N(6)-H(6A)···Cl(1)[b]	0.86	2.3	3.0888(13)	151.9

Symmetry code: [a] -x+1,-y+1,-z+1 [c] -x+2, y-1/2, -z+3/2
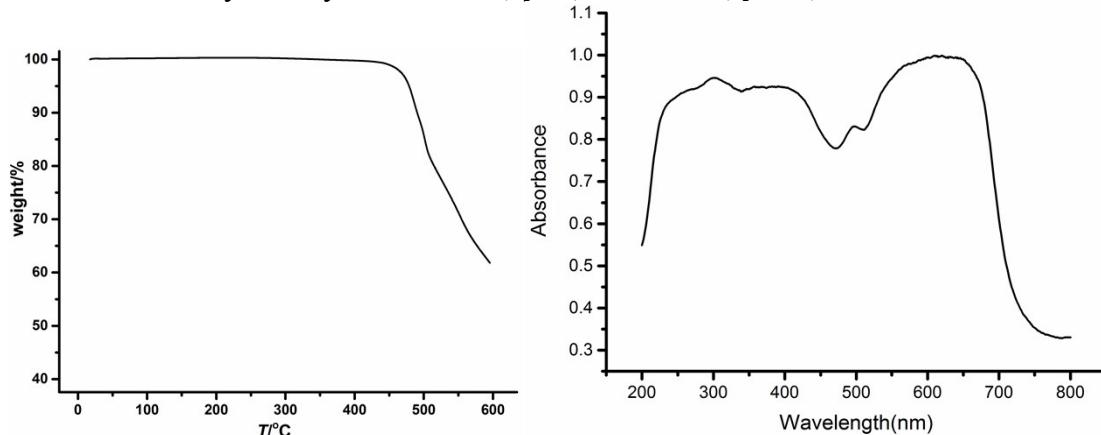
Fig S3 The TGA (left) and UV-Vis spectrum (right) of **1.**

Simulation of Coupling constant from $\chi_M T$ *vs.T* curve in detail (alternative dinuclear-Co$_2$ chain model without considering magnetic anisotropy, using software Origin):

1. Deduction of the *J* (coupling constant) unit

k or k_B is Boltzmann constant, *k*= 1.3806503 × 10^{-23} J/K

1 cm^{-1}= 1.986× 10^{-23} J=1.441 K

So, *k*=1.3806503×10^{-23}J/K=1.3806503×10^{-23}/(1.986×10^{-23})cm^{-1}/K=0.69519149cm^{-1}/K

If $1/k$=1.441 K/cm^{-1}, the unit of J is cm^{-1}

If $1/k$=1.441 K/cm^{-1}=1 cm^{-1}/cm^{-1}=1, the unit of J is K

2. χ_d (molar magnetic susceptibility of Co2 dimmer):

$$\chi_d = \frac{Ng^2\beta^2}{3kT}S_d(S_d+1)$$

$$S_d(S_d+1)=6\times\frac{\exp(2J_d/kT)+5\exp(6J_d/kT)+14\exp(12J_d/kT)}{1+3\exp(2J_d/kT)+5\exp(6J_d/kT)+7\exp(12J_d/kT)}=\frac{\sum S_T(S_T+1)(2S_T+1)\exp(-E_s/kT)}{\sum(2S_T+1)\exp(-E_s/kT)}$$

$$\chi_d = \frac{2Ng^2\beta^2}{kT}\frac{\exp(2J_d/kT)+5\exp(6J_d/kT)+14\exp(12J_d/kT)}{1+3\exp(2J_d/kT)+5\exp(6J_d/kT)+7\exp(12J_d/kT)}$$

3. For alternative chain by Rojo formula (Inorg. Chem. 1997, 36, 677)

$$\chi = \frac{Ng^2\beta^2}{3kT}\frac{1+u_1+u_2+u_1u_2}{1-u_1u_2}S(S+1)$$

u_1=coth$[J_1S(S+1)/kT]$-$kT/J_1S(S+1)$, u_2=coth$[J_2S(S+1)/kT]$-$kT/J_2S(S+1)$

4. For alternative chain of Co(II) dimmer in our system:

we can get the following equation:

$$\chi = \frac{Ng^2\beta^2}{3kT}\frac{1+u_1+u_2+u_1u_2}{1-u_1u_2}S_d(S_d+1)$$

$$S_d(S_d+1) = 6\times\frac{\exp(2J_1/kT)+5\exp(6J_1/kT)+14\exp(12J_1/kT)}{1+3\exp(2J_1/kT)+5\exp(6J_1/kT)+7\exp(12J_1/kT)}$$

u_1=coth$[J_2S_d(S_d+1)/kT]$-$kT/J_2 S_d(S_d+1)$, u_2=coth$[J_3S_d(S_d+1)/kT]$-$kT/J_3S_d(S_d+1)$

5. The function file for fitting in OriginPro2021 with the J unit in cm^{-1}, in two column

[General Information]

Function Name = Co2alternativechain

Brief Description =

Function Source = N/A

Number Of Parameters = 7

Function Type = User-Defined

Function Form = Equations

Path =

Number Of Independent Variables = 1

Number Of Dependent Variables = 1

FunctionPrev = NewFunction1

[Fitting Parameters]

Names = J2,g,J3,J1,zJ,Theta,TIP

Initial Values = --(V)

Meanings = ?

Lower Bounds = --(X, OFF)

Upper Bounds = --(X, OFF)

Naming Method = User-Defined

Number Of Significant Digits =

Unit =

[Independent Variables]

T =

[Dependent Variables]

ChimT =

[Formula]

double k=0.69503887;

double NB2=0.260727165;

double x=1/(k*T);

double u1,u2;

double temp3=6*(exp(2*x*J1)+5*exp(6*x*J1)+14*exp(12*x*J1))/(1+3*exp(2*x*J1)+5*exp(6*x*J1)+7*exp(12*x*J1));

u1=cosh(x*J2*temp3)/sin(x*J2*temp3)-1/(x*J2*temp3);

u2=cosh(x*J3*temp3)/sin(x*J3*temp3)-1/(x*J3*temp3);

double chi=0.125*g*g*(1+u1+u2+u1*u2)/(1-u1*u2)*temp3/(T-Theta);

double chid=1/chi-2.0*zJ/(NB2*g^2);

ChimT=T*(1/chid+TIP);;

[Initializations]

[After Fitting]

[Controls]

General Linear Constraints = 0

Initialization Scripts = 0

Scripts After Fitting = 0

Number Of Duplicates = N/A

Duplicate Offset = N/A

Duplicate Unit = N/A

Generate Curves After Fitting = 1

Curve Point Spacing = Uniform on X-Axis Scale

Generate Peaks After Fitting = 1

Generate Peaks During Fitting = 1

Generate Peaks with Baseline = 1

Paste Parameters to Plot After Fitting = 1

Paste Parameters to Notes Window After Fitting = 1

Generate Residuals After Fitting = 0

Keep Parameters = 0

Compile On Param Change Script = 1

Enable Parameters Initialization = 1

[Compile Function]

Compile = 1

Compile Parameters Initialization = 1

OnParamChangeScriptsEnabled = 0.

Simulation of Coupling constant from $\chi_M T$ *vs.* T curve using software Magpack [1](ring model of chain compound considering magnetic anisotropy):

Scheme S1. The ring-model of the chain compounds to calculate the coupling constant using the software Magpack. [1]

The Spin Hamiltonian Equation of ring-model of the chain compound (Scheme S1) as follows :
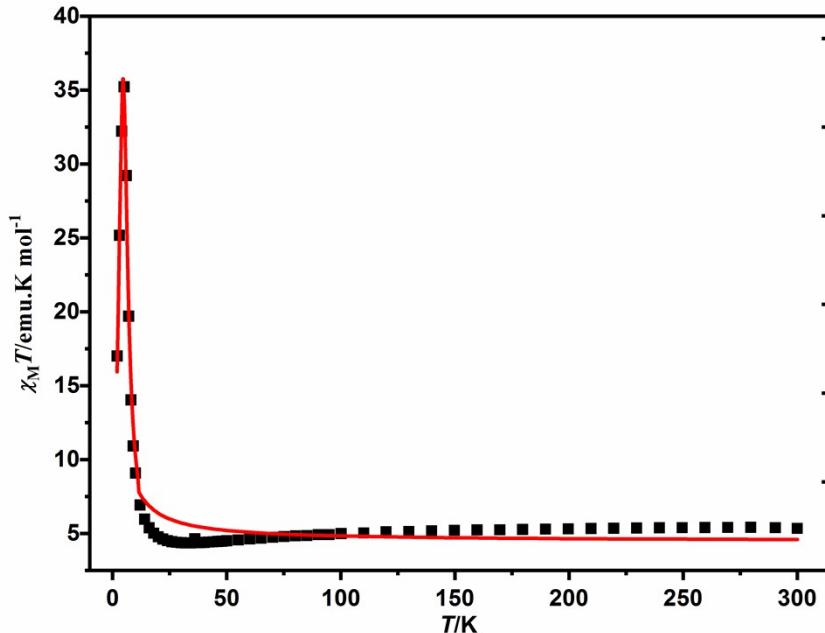
$$H = -2J_1 \left(\vec{S_1}\vec{S_2} + \vec{S_3}\vec{S_4} + \vec{S_5}\vec{S_6} + \vec{S_7}\vec{S_8} + \vec{S_9}\vec{S_{10}} + \vec{S_{11}}\vec{S_{12}} \right)$$

$$- 2J_2 \left(\vec{S_2}\vec{S_3} + \vec{S_6}\vec{S_7} + \vec{S_{10}}\vec{S_{11}} \right) - 2J_3 \left(\vec{S_4}\vec{S_5} + \vec{S_8}\vec{S_9} + \vec{S_{12}}\vec{S_1} \right)$$

$$- 2J_x \left(\sum_{i=1}^{11} \vec{S_i^x}\vec{S_{i+1}^x} + \vec{S_{12}^x}\vec{S_1^x} \right) - 2J_y \left(\sum_{i=1}^{11} \vec{S_i^y}\vec{S_{i+1}^y} + \vec{S_{12}^y}\vec{S_1^y} \right)$$

$$- 2J_z \left(\sum_{i=1}^{11} \vec{S_i^z}\vec{S_{i+1}^z} + \vec{S_{12}^z}\vec{S_1^z} \right)$$

$$+ \mu_B H_z \left[g_{z1} \left(\vec{S_1^z} + \vec{S_4^z} + \vec{S_5^z} + \vec{S_8^z} + \vec{S_9^z} + \vec{S_{12}^z} \right) \right.$$

$$\left. + g_{z2} \left(\vec{S_2^z} + \vec{S_3^z} + \vec{S_6^z} + \vec{S_7^z} + \vec{S_{10}^z} + \vec{S_{11}^z} \right) \right] + D \sum_{i=1}^{12} (\vec{S_i^z})^2$$

Fig S4 The best fit of $\chi_M T$ vs. T curve using software Magpack [1] (the black square is the experimental $\chi_M T$ vs. T curve and the red solid line is the best fit by the ring-model of chain compound)

The input files of parani21

PARAMETER (NUM=12)   ! number of centers (<=14)

C

PARAMETER (IDTOT = 1703636) ! dimension of full energy matrix

PARAMETER (IDTOTF= 1) ! [If IEIG=2 then IDTOTF=IDTOT; else =1]

C

```
      PARAMETER (IUNI=2)  ! units (1=K,
2=meV, 3=cm-1)
  C

      PARAMETER (IISO=1)   ! isotropic
exchange [1(yes)/0(no)]
  C

      PARAMETER (IANL=1)    ! local
anisotropy [1(yes)/0(no)]
  C

      PARAMETER    (IANI=0)       !
anisotropic exchange [1(yes)/0(no)]
  C

      PARAMETER (ISUS=1)  ! Magnetic
susceptibility
  C

      PARAMETER (ICAL=0)  ! Specific
heat
  C

      PARAMETER    (IMAG=1)       !
Magnetization
  C

      PARAMETER (ISPI=0)   ! write the
base functions [1(yes)/0(no)]
  C

      PARAMETER (IEIG=0)    ! write
eigenvalues
  C
[no(0)/yes(1)/yes+eigenvect(2)]
  C
  C
  C-------------------------------
  C* The following parameter is defined to
minimize underflow problems
      PARAMETER (EPS   = 1.D-12)
```

The input files of parani22

```
  C**   SPIN  OF  EACH  CENTER.
ISN(I)=2S; I<=14
  C
      ISN(1) = 3
      ISN(2) = 3
      ISN(3) = 3
      ISN(4) = 3
      ISN(5) = 3
      ISN(6) = 3
      ISN(7) = 3
```

```
      ISN(8) = 3
      ISN(9) = 3
      ISN(10)= 3
      ISN(11)= 3
      ISN(12)= 3
      ISN(13)= 0
      ISN(14)= 0
  C

  C****  NON  ZERO  EXCHANGE
PARAMETERS BETWEEN CENTERS I
AND J (I<J)
  C**   ISOTROPIC   EXCHANGE
PARAMETERS: CONEX(I,J,1) = K
  C
      CONEX(1,2,1)= 0.15D0
      CONEX(2,3,1)= 6.150D0
      CONEX(3,4,1)= 0.15D0
      CONEX(4,5,1)= 0.100D0
      CONEX(5,6,1)= 0.15D0
      CONEX(6,7,1)= 6.150D0
      CONEX(7,8,1)= 0.15D0
      CONEX(8,9,1)= 0.100D0
      CONEX(9,10,1)= 0.15D0
      CONEX(10,11,1)= 6.150D0
      CONEX(11,12,1)= 0.150D0
      CONEX(12,1,1)= 0.10D0


  C
  C**  BIQUADRATIC  EXCHANGE
PARAMETERS: CONEX(I,J,2) = K
  C
      CONEX(1,2,2)= 0.0D0
  C
  C**    ANISOTROPIC  EXCHANGE
PARAMETERS:
  C        CONEX (I,J,3)=JX, CONEX
(I,J,4)=JY, CONEX (I,J,5)=JZ
  C
      CONEX(1,2,3)= -0.10D0
      CONEX(2,3,3)= -0.1D0
      CONEX(3,4,3)= -0.10D0
      CONEX(1,2,4)= -0.10D0
      CONEX(2,3,4)= -0.1D0
```

```
      CONEX(3,4,4)= -0.10D0
      CONEX(1,2,5)= 0.10D0
      CONEX(2,3,5)= 0.10D0
      CONEX(3,4,5)= 0.10D0
   C
   C**       LOCAL     ANISOTROPIC
 PARAMETERS:
   C
      ANILOD(1)  = -0.0100D0
      ANILOD(2)  = -0.5200D0
      ANILOD(3)  = -0.5200D0
      ANILOD(4)  = -0.010D0
      ANILOD(5)  = -0.0100D0
      ANILOD(6)  = -0.5200D0
      ANILOD(7)  = -0.5200D0
      ANILOD(8)  = -0.010D0
      ANILOD(9)  = -0.0100D0
      ANILOD(10)  = -0.5200D0
      ANILOD(11)  = -0.5200D0
      ANILOD(12)  = -0.010D0
   C
      ANILOE(1)  =  0.00D0
      ANILOE(2)  =  0.00D0
      ANILOE(3)  =  0.00D0
      ANILOE(4)  =  0.00D0
   C
   C** A-3) G PARAMETERS (GX=GY)
   C
      GX(1) = 0.0d0
      GY(1) = GX(1)
      GZ(1) = 2.70d0
      GX(2) = 0.0d0
      GY(2) = GX(2)
      GZ(2) = 3.7d0
      GX(3) = 0.0d0
      GY(3) = GX(3)
      GZ(3) = 3.7d0
      GX(4) = 0.0d0
      GY(4) = GX(4)
      GZ(4) = 2.7d0
      GX(5) = 0.0d0
      GY(5) = GX(1)
```

```
      GZ(5) = 2.70d0
      GX(6) = 0.0d0
      GY(6) = GX(2)
      GZ(6) = 3.7d0
      GX(7) = 0.0d0
      GY(7) = GX(3)
      GZ(7) = 3.7d0
      GX(8) = 0.0d0
      GY(8) = GX(4)
      GZ(8) = 2.7d0
      GX(9) = 0.0d0
      GY(9) = GX(1)
      GZ(9) = 2.70d0
      GX(10) = 0.0d0
      GY(10) = GX(2)
      GZ(10) = 3.7d0
      GX(11) = 0.0d0
      GY(11) = GX(3)
      GZ(11) = 3.7d0
      GX(12) = 0.0d0
      GY(12) = GX(4)
      GZ(12) = 2.7d0


   C
   C
   C**              MAGNETIZATION
 PARAMETERS
   C
   C    ANGLE STEP TO INTEGRATE
 OVER ALL DIRECCTONS (DEG)
      IANG = 50
   C
   C        MAXIMUM  VALUE  OF
 MAGNETIC  FIELD  (ICAMMAX/100
 TESLAS)
      ICAMMAX = 500
   C
   C    STEP IN MAGNETIC FIELD TO
 PLOT M VS H (ICAMSTP/100 TESLAS)
      ICAMSTP = 20
   C
   C   TEMPERATURE  (K)
      TEMP = 2.0D0
```

C

C SHOW 0=AVERAGED, PAPALLEL AND PERPENDICULAR MAGNETIZATION

C 1=AVERAGED AND ALL CALCULATED CONTRIBUTIONS

 ISHOW = 1

C

C

C** SUSCEPTIBILITY

C

C INITIAL TEMPERATURE (K)

 TEMP1 = 2.0D0

C

C FINAL TEMPERATURE (K)

 TEMP2 = 300.0D0

C

C NUMBER OF POINTS

 ISTEPTEMP = 100

C

C MAGNETIC FIELD (CAMPO/100 TESLAS)

 CAMPO = 10.D0

DFT calculations on the magnetic coupling constants.

To estimate the exchange coupling constants between the Co^{2+} ions, calculations based on the density function theory integrating with the broken-symmetry approach (BS)[2, 3] were carried out for **1**. The initial structure was the periodic model of two tetramers in one lattice unit cell (Fig. S5) extracted from cif file. The exchange coupling constants J (Table S2) have been evaluated by calculating the energy difference between the high-spin state (E_{HS}) and the broken symmetry state (E_{BS}). The phenomenological spin Hamiltonian is defined as: $H = -2J S_1 S_2$. Based on this spin Hamiltonian, the coupling constant J can be extracted from the following equation: $J = (E_{BS}-E_{HS})/(4S_1S_2+2S_2)$. For our system, $S_1 = S_2 = 3/2$, thus, $J = (E_{BS}-E_{HS})/12$.

a) HS

$E_{HS}=(-4J_1-2J_2-4J_3) \times 12$

eq1

b) BS_1

$E_{BS1}=(-3J_1-2J_2-3J_3) \times 12$

eq2

eq2-eq1: $E_{BS1}-E_{HS}=\Delta E_1 =(J_1+J_3) \times 12$ so we get $J_1+J_3=\Delta E_1/12$

c)   BS$_2$

$E_{BS2}=(-3J_1-J_2-3J_3) \times 12$

eq3

eq3-eq1: $E_{BS2}-E_{HS}=\Delta E_2 =(J_1+J_2+J_3) \times 12$ so we get $J_1+J_2+J_3=\Delta E_2/12$

d)   BS$_3$

$E_{BS3}=(-4J_1-J_2-2J_3) \times 12$

eq4

eq4-eq1: $E_{BS3}-E_{HS}=\Delta E_3 =(J_2+2J_3) \times 12$ so we get $J_2+2J_3=\Delta E_3/12$
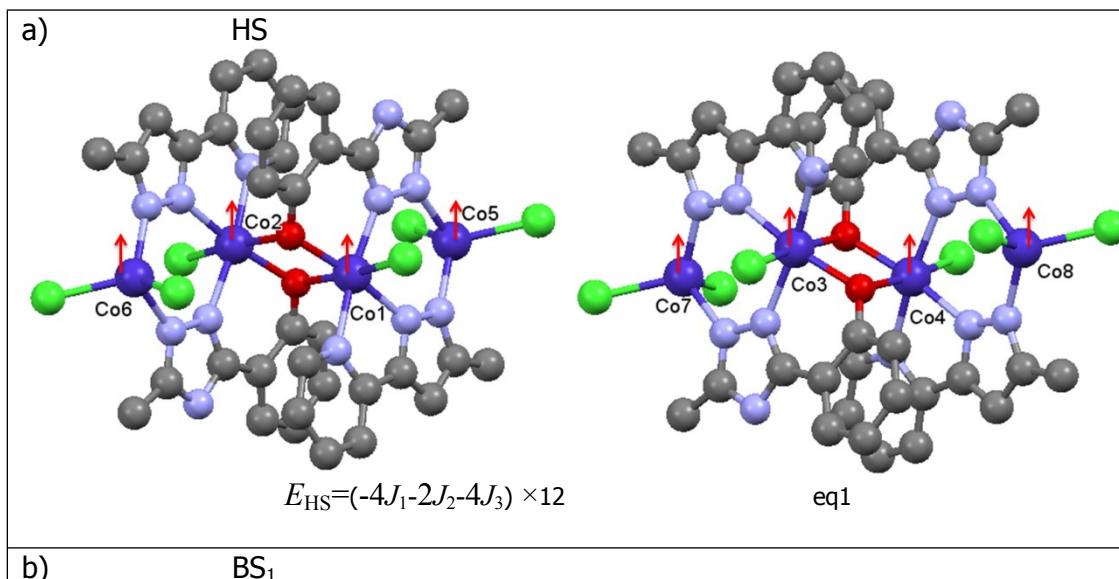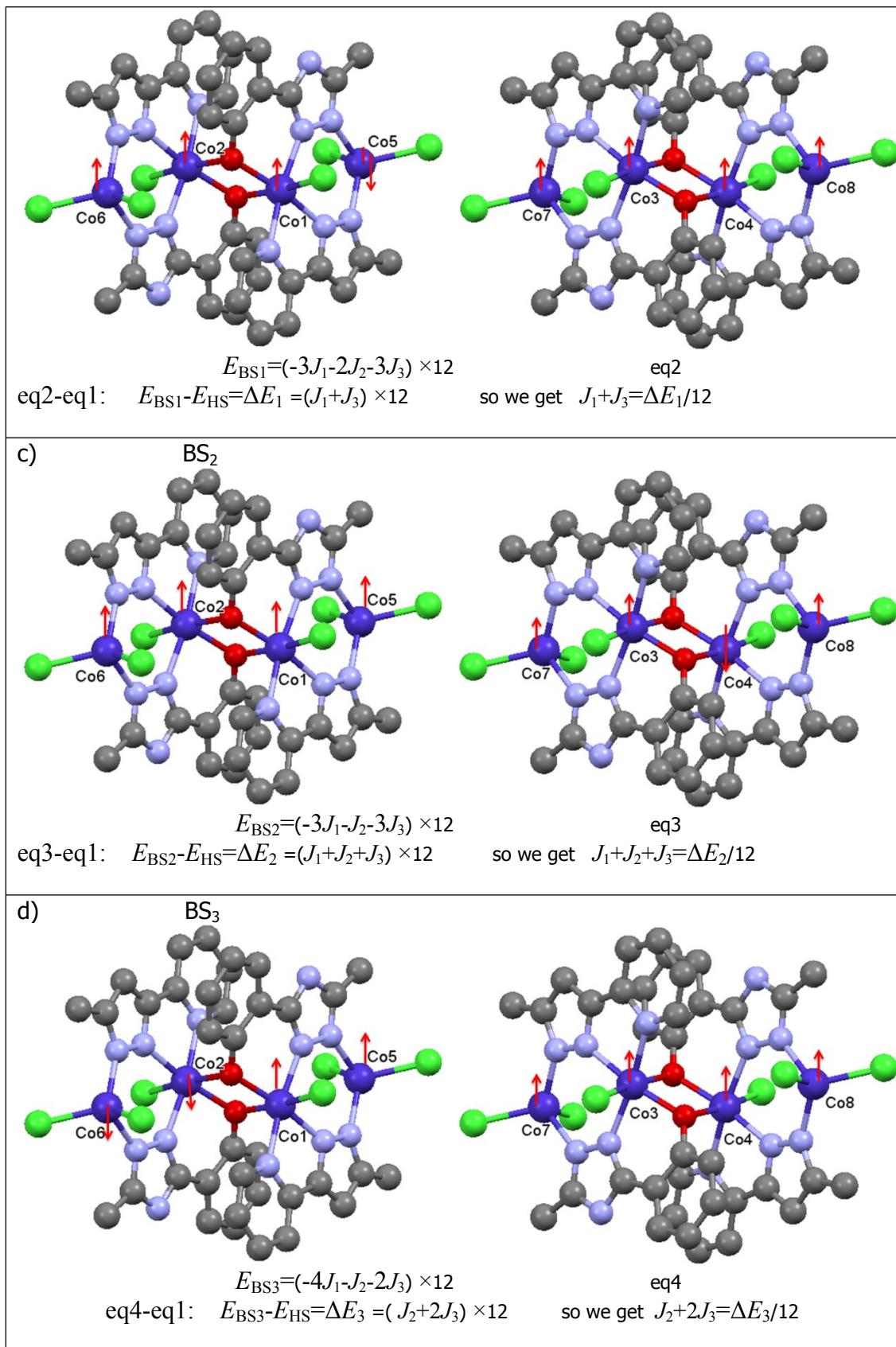
Fig. S5. The spin configurations of the two tetramers in one lattice unit cell, the direction of the arrows representing the spin orientation: a) all the spins up in the

high-spin state (HS); b) only the spin of Co5 down in the first broken-symmetry state (BS1); c) only the spin of Co4 down in the second broken-symmetry state (BS2); d) only the spin of Co2 and Co6 down in the third broken-symmetry state (BS3), .

All calculations (including optimizations and energy evaluations) were performed on the Quantum Espresso package (QE) Version 6.5,[4, 5] using the PBE+U+D3 [6]scheme with U =2.29 eV for the d orbitals of cobalt referring to iron.[7] The spin unrestricted formalism, the D3 correction of Grimme, Vanderbilt pseudopotentials,[8] and a Γ-point sampling of the Brillouin zone was set up. The computation of HS and BS state was performed by successive variable-cell geometry relaxations (vc-relax) at the solid-state until the minima were obtained. The lattice parameters and the atomic positions are optimized simultaneously. The convergence criterion was set at atomic forces smaller than 1×10^{-5} atomic units. In these calculations, the number of plane waves was kept constant at a kinetic energy cutoff of 70 and 560 Ry for ecutwfc and ecutrho, respectively. This large cutoff ensures that artifacts originated in the change of unit-cell volume (i.e., Pulay stress) are negligible. The spin state of the cobalt atoms is set by defining an appropriate initial guess (HS or BS) that is maintained along the optimization. The final unit cell parameters and coordinates are provided in Computational Data file.

Table S2. DFT calculation results for the molecules in one unit cell

	E(Ry)	ΔE (cm^{-1}) [a]	$\Delta E/12$(cm^{-1})	Coupling strength(cm^{-1})
HS	-4090.775981			
BS1	-4090.793857	-1962.80 (ΔE_1)	-163.57	J_1+J_3
BS2	-4090.787867	-1305.10 (ΔE_2)	-108.76	$J_1+J_2+J_3$
BS3	-4090.787536	-1268.80 (ΔE_3)	-105.73	J_2+2J_3
J_1=-83.30, J_2=54.81, J_3=-80.27				

[a]$\Delta E = E_{BS}-E_{HS,\ KJ/mol}$= Ry/2*627.51*4.184; cm^{-1}=$_{KJ/mol}$/(6.02*10^{-23})/(1.986*10^{-23})*1000

First of all, here it should be emphasized that we do not know what is the proper U values for the cobalt in this magnetic system and there is no report involving this value. Therefore, we have to choose the U values from iron.[7] Although the U values influent the energy difference between the HS and BS state, the change is almost linear and below 10 KJ/mol (836 cm^{-1}) per 0.2 eV of U (Fig. S6.). It is presumed that change value is x cm^{-1}. We found that the selection of U values will not impact J_2,

$J_2= (J_1+J_2+J_3)-(J_1+J_3) = (\Delta E_2+x)- (\Delta E_1+x) = \Delta E_2-\Delta E_1$

However, the J_1 and J_3 will be impacted by the half of x:

$J_3= [(J_2+2J_3) − J_2]/2= [(\Delta E_3+x)-J_2]/2 =(\Delta E_3-\Delta E_2+\Delta E_1)/2+x/2$

$J_1=(J_1+J_3) − J_3= (\Delta E_1+x)-[(\Delta E_3-\Delta E_2+\Delta E_1)/2+x/2]= [(-\Delta E_3+\Delta E_2+\Delta E_1)/2 +x/2$

Perhaps, the calculations are not accurate, but at least we can confirm qualitatively the exchange coupling constants between the Co^{2+} ions.
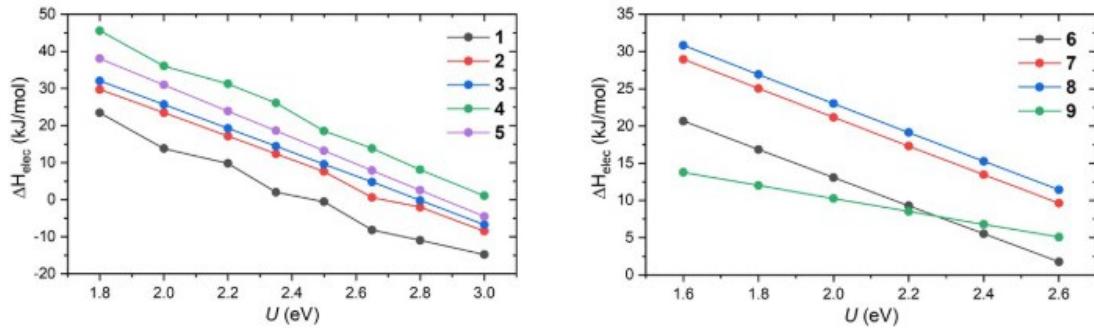
Fig. S6. Evolution of ΔH_{elec} with U for (left) Fe^{II} and (right) Fe^{III} compounds (copied from ref. [7]).

Secondly, we need to emphasize that the calculated magnetic interactions transferred by the three types of bridge here represent only an approximation of the magnetic interactions between the Co^{2+} centers. Several other possible contributions to the overall interactions, such as the nearest magnetic interactions, dipole-dipole interactions, and magnetic interactions transferred through the hydrogen bonds, are included into the covalent bridge interactions. Also, we don't consider the contribution of the orbital-spin coupling.
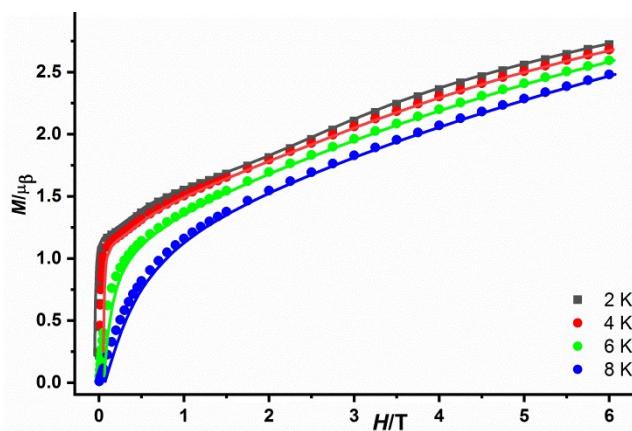
Fig. S7 Isothermal field-dependence of the magnetization per Co2 at multiple temperatures for **1.** The solid lines are the best fits by the software Magpack at each temperature. The parameters for the best fit are $J_1 = +0.10$ cm^{-1}; $J_2 = +11.15$ cm^{-1}; $J_3 =$

+0.10 cm^{-1}; $J_x=J_y$ =-8.10cm^{-1}; J_z =1.50 cm^{-1}; D_1 = -0.01; D_2 = -6.52; E_1 = -0.01; E_2 = -0.10; g_1 = 2.4; g_2 = 3.4.

Dynamic magnetic properties
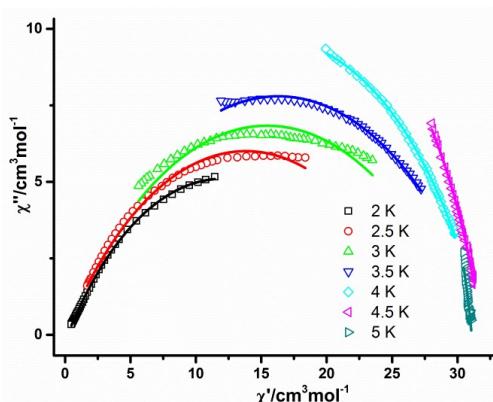
Fig. S8. The Cole-Cole plots of **1** at various temperatures, red lines are the best fits.

Table S3 The α values from the fitting of the Cole-Cole plots of **1**

1	T/K	2	2.5	3	3.5	4	4.5
	α	0.48	0.48	0.47	0.43	0.31	0.17

References

1 J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *J. Comput. Chem.*, 2001, **22**, 985-991.
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