Structures and magnetic anisotropies of two seven-coordinate Co(II)-nitrate complexes showing slow magnetic relaxation

Wei Lv,[a] Lei Chen,[b] Xue-Tai Chen,*[a] Hong Yan,*[a] Zhenxing Wang,*[c] Zhong-Wen Ouyang,[c] Zi-Ling Xue[d]

[a]*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China. Email: xtchen@nju.edu.cn; hyan1965@nju.edu.cn.*

[b]*School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, P. R. China.*

[c]*Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology, Wuhan 430074, China. Email: zxwang@hust.edu.cn.*

[d]*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA.*

Electronic Supplementary Information

Table S1 Summary of seven-coordinated Co(II)-SIMs with non-pentagonal bipyramid geometry

Complex	Vertex	Geometry[a]	CShM value	D [b] / cm^{-1}	E [b] / cm^{-1}	U_{eff}
Co(tmpdc[c])$(NO_3)_2$(this work)	N_3O_4	COC-7	2.437	4.73, 3.65, ─	0.96, 0.70, ─	─
$(PPh_4)_2[Co(NO_3)_4]\cdot CH_2Cl_2$[1]	O_7	IR[d]	─[d]	12.85, 10.90, 11.3	3.60, 1.56, -0.4	22.5 cm^{-1}
$(MePh_3P)_2[Co(NO_3)_4]$[1]	O_7	IR[d]	─[d]	23.21, 12.74, 23.1	0.64, 2.20, -0.9	26.6 cm^{-1}
[(L1[c])$Co(NO_3)_2$][2]	N_3O_4	CTPR-7[e]	2.040[e]	-41.4, ─, -7.23	4.50, ─, 1.32	─
[Co(L2[c])]Cl_2[3]	N_7(pseudo)	COC-7	1.18	9.20, ─, 9.8	0.018, ─, 0.294	9.2 cm^{-1}
[Co(L2[c])]Br_2[3]	N_7(pseudo)	COC-7	1.23	2.12, ─, 5.9	~0, ─, ~0	─
[Co(L2[c])]I_2[3]	N_7(pseudo)	COC-7	1.30	3.61, ─, 12.4	1.44, ─, 0.074	─
[Co(L2[c])]$(ClO_4)_2$[3]	N_7(pseudo)	COC-7	1.49	4.21, ─, 15.9	0.25, ─, 0.032	─
[Co(L3[c])$_4$]$(ClO_4)_2$[4]	N_7	CTPR-7	4.033	25.30, ─, 26.7	-9.09, ─, -8.2	61.30 K
[Co(L4[c])]$(BF_4)_2$[5]	N_7	CTPR-7	2.715	13.1, 13.21, 17.1	0.03, 0.7, -2.7	39.7 K
[Co(L4[c])]($ClO_4)_2\cdot H_2O$[6]	N_7	CTPR-7	2.538	15.4, 15.5, ─	0.07, 0.93, ─	─
[Co(L4[c])]$(PF_6)_2$[6]	N_7	COC-7	2.232, 2.589	10.0, 10, ─	0.07, 2.38, ─	9.1 K
[Co(L4[c])]$(BPh_4)_2$[6]	N_7	CTPR-7	2.752	14.6, 14.5, ─	0.06, 0.48, ─	4.8 K

a. COC-7 = capped octahedron, CTPR-7 = capped trigonal prism, IR = irregular geometry

b. The D and E values listed in this Table are obtained by fitting of PHI, HFEPR data and calculations.

c. The structures of ligands are shown in Fig. S1 below.

d. Irregular geometry due to that the CShM values of these two complexes relative to all ideal seven-coordinate geometries are too large (above 15).

e. We analysed the cif file provided with Shape 2.1 and the results demonstrate that it has a capped trigonal prismatic geometry instead of pentagonal bipyramid.

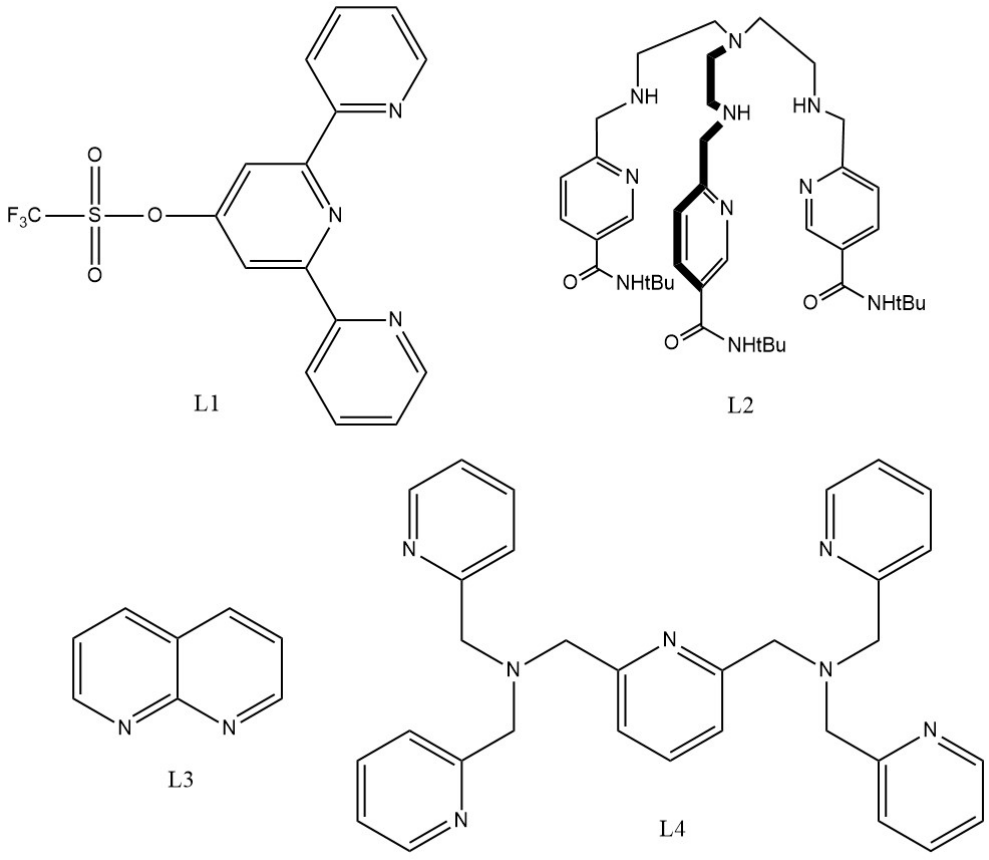


Fig. S1 Structures of the ligands in Table S1

Table S2 The results of the continuous shape measure (*CShM*) analyses of $[(L1)Co(NO_3)_2]$

Seven-vertex		$[(OTftpy)Co(NO_3)_2]$
Deviation parameter	Heptagon	34.741
	Hexagonal pyramid	20.354
	Pentagonal bipyramid	7.400
	Capped octahedron	3.085
	Capped trigonal prism	2.040
	Johnson pentagonal bipyramid	10.623
	Johnson elongated triangular pyramid	17.312

Table S3 Summary of crystal data and refinement for **1** and **2**

	1	**2**
Molecular formula	$C_{11}H_{15}N_5O_8Co$	$C_{13}H_{18}N_6O_6S_2Co$
CCDC no	2261409	2261435
Formula weight	404.21	477.38
Temperature	296(2)	296(2)
Crystal system	Monoclinic	Triclinic
Space group	P 2_1/n	P $\bar{1}$
a / Å	7.6026(3)	9.7797(9)
b / Å	15.4311(6)	10.3740(11)
c / Å	13.8687(6)	10.8769(9)
α (°)	90	92.616(4)
β (°)	96.588(2)	103.465(3)
γ (°)	90	112.947(3)
V / Å^3	1616.28(11)	976.72(16)
Z	4	2
D_{calc}, g/cm^3	1.661	1.623
μ / mm^{-1}	1.115	1.136
F (000)	828.0	490.0
θ range [°]	1.982/25.997	2.350/27.239
Reflns collected	13059	8633
R_{int}	0.0441	0.0329
Indep. reflns	3162	1869
Data/restr./paras	3162/4/230	1869/203/149
Goodness-of-fit on F^2	1.046	1.046
R_1, wR_2 [I > 2σ(*I*)][a]	0.0301/0.0748	0.0450/0.1160
R_1, wR_2 [all data][a]	0.0336/0.0772	0.0496/0.1204

[a]$wR_2 = [\Sigma[w(F_o^2–F_c^2)^2]/\Sigma[w(Fo^2)^2]]^{1/2}$, $R_1 = \Sigma||F_o|–|F_c||/\Sigma|F_o|$.

Table S4 Selected bond lengths (Angstroms) and angles (degree) for **1** and **2**

1		**2**	
Co1-N2	2.0648(1)	Co1-N2	2.0979(1)
Co1-O1	2.1853(1)	Co1-O1	2.4768(1)
Co1-O2	2.2400(1)	Co1-O2	2.1294(1)
Co1-O4	2.1452(1)	Co1-O4	2.1318(1)
Co1-O5	2.1716(1)	Co1-O5	2.2688(1)
Co1-O7	2.1757(1)	Co1-S1	2.4474(5)
Co1-O8	2.1879(1)	Co1-S2	2.4380(5)
N2-Co1-O1	90.65(5)	N2-Co1-O1	76.65(5)
N2-Co1-O2	112.98(5)	N2-Co1-O2	131.66(6)
N2-Co1-O4	162.43(5)	N2-Co1-O4	146.45(6)
N2-Co1-O5	114.16(5)	N2-Co1-O5	89.02(6)
N2-Co1-O7	75.08(5)	N2-Co1-S1	83.11(4)
N2-Co1-O8	74.06(5)	N2-Co1-S2	83.40(4)
O1-Co1-O2	57.83(5)	O1-Co1-O2	55.01(5)
O1-Co1-O4	91.26(5)	O1-Co1-O4	136.15(5)
O1-Co1-O5	149.08(5)	O1-Co1-O5	165.64(5)
O1-Co1-O7	83.23(5)	O2-Co1-O4	81.53(6)
O1-Co1-O8	122.41(5)	O2-Co1-O5	139.31(6)
O2-Co1-O4	82.61(5)	O4-Co1-O5	57.94(6)
O2-Co1-O5	121.33(5)	S1-Co1-O1	88.75(4)
O2-Co1-O7	139.44(5)	S1-Co1-O2	94.39(4)
O2-Co1-O8	77.58(5)	S1-Co1-O4	101.31(4)
O4-Co1-O5	59.49(4)	S1-Co1-O5	90.54(5)
O4-Co1-O7	87.80(5)	S2-Co1-O1	86.70(4)
O4-Co1-O8	118.98(5)	S2-Co1-O2	93.46(4)
O5-Co1-O7	85.66(5)	S2-Co1-O4	90.79(4)
O5-Co1-O8	83.73(5)	S2-Co1-O5	90.71(5)
O7-Co1-O8	139.56(5)	S1-Co1-S2	166.427(1)

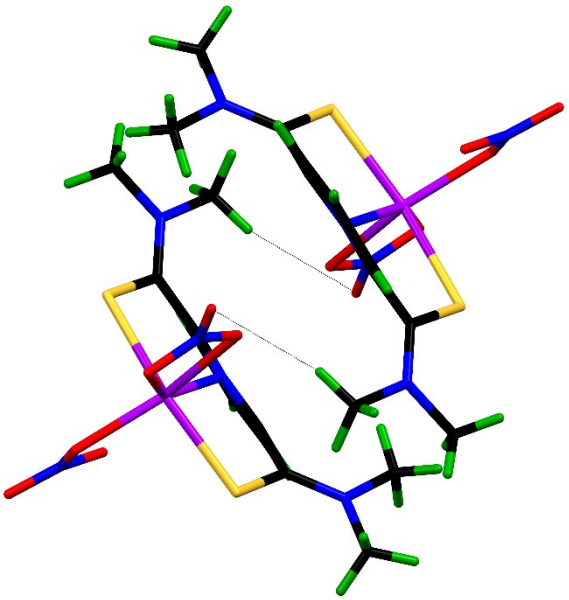


Fig. S2 The central symmetric structure of **2** in cell unit

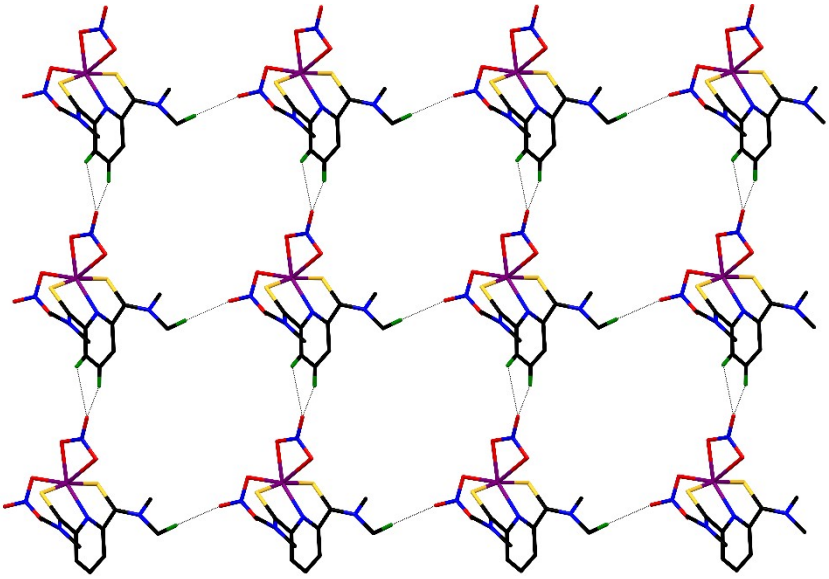
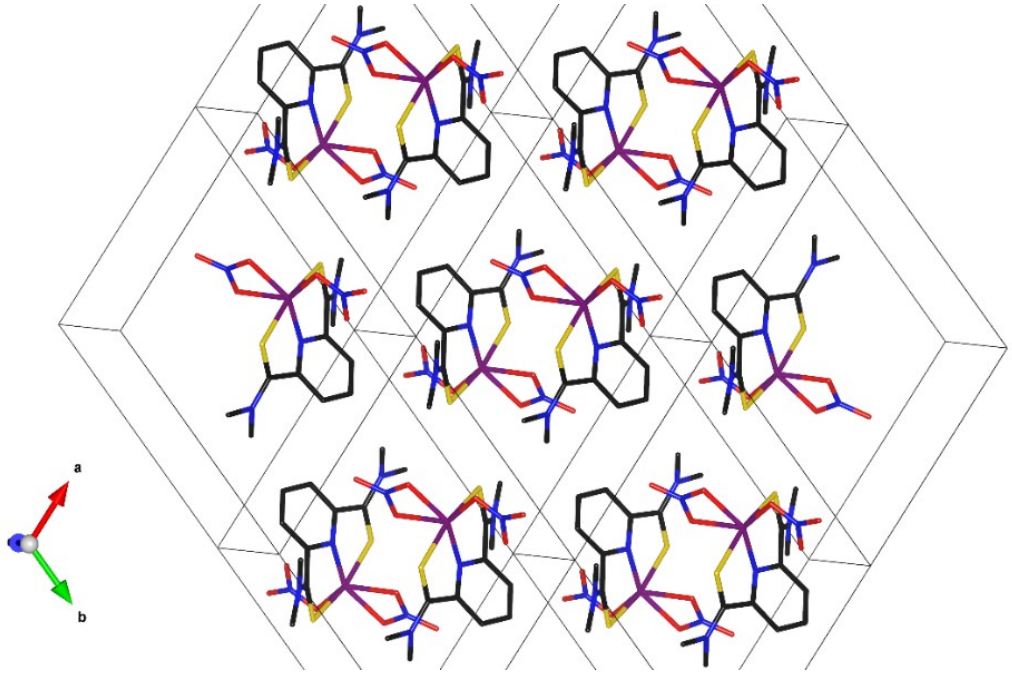
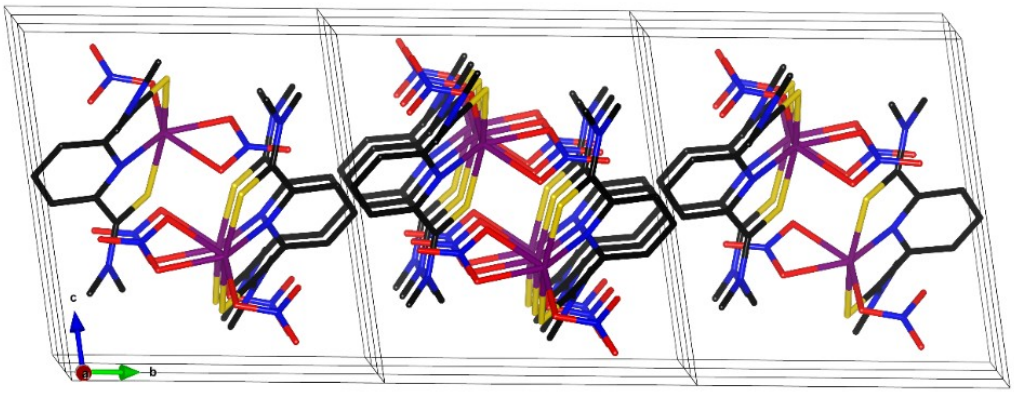


Fig. S3 The 2-D sheet formed by intermolecular H-bonding in **2**. The hydrogens other than those involved in H-bonding are omitted for clarity.



(a)



(b)

Fig. S4 The double-decker structure of **2** formed by cell unit (drawn with VESTA Program[7]). The H atoms are hidden for clarity.

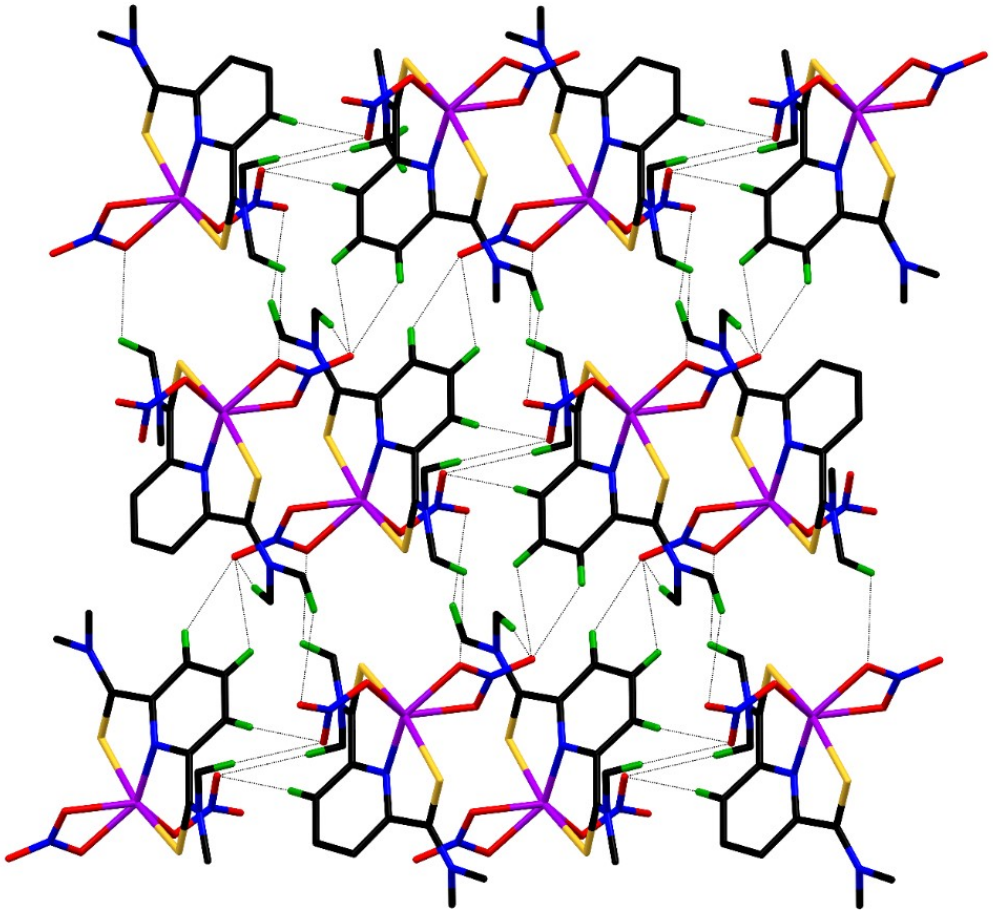


Fig. S5 The H-bonding in 3-D structure of complex **2**

Table S5 The results of the continuous shape measure (*CShM*) analyses of **1** and **2** by SHAPE software.

Seven-vertex		**1**	**2**
Deviation parameter	Heptagon	35.911	32.580
	Hexagonal pyramid	17.954	22.407
	Pentagonal bipyramid	8.075	2.217
	Capped octahedron	2.437	7.434
	Capped trigonal prism	3.134	5.655
	Johnson pentagonal bipyramid	11.435	7.415
	Johnson elongated triangular pyramid	16.927	21.426

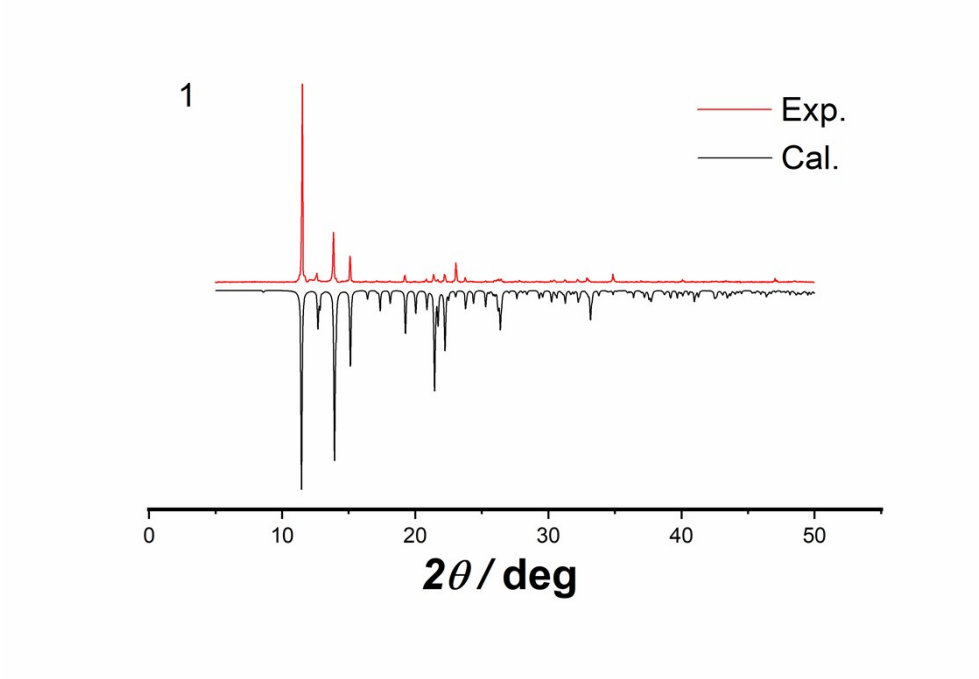


Fig. S6 XRD patterns for **1** (The red line is PXRD experimental pattern and the black line are calculated from single-crystal structure)

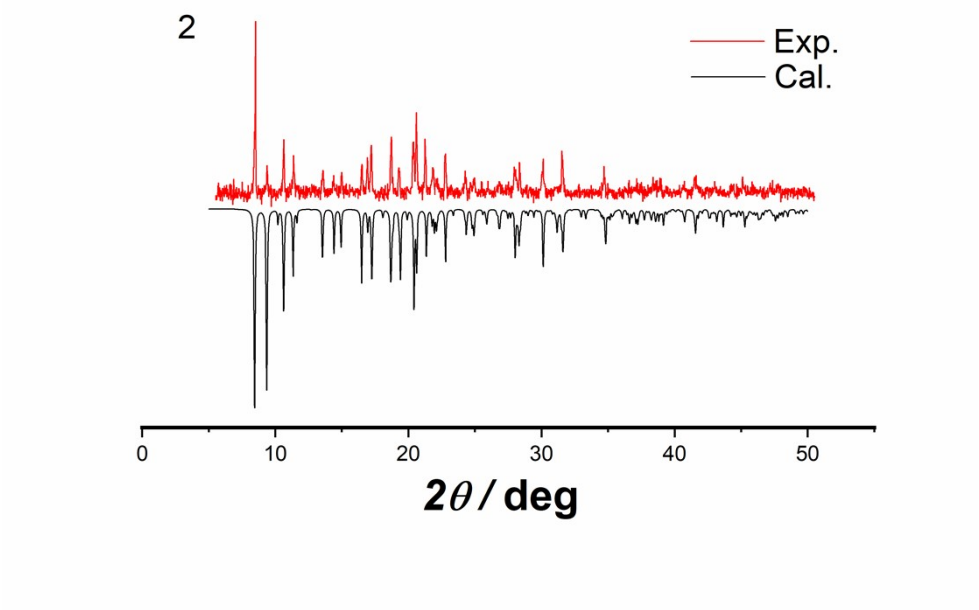
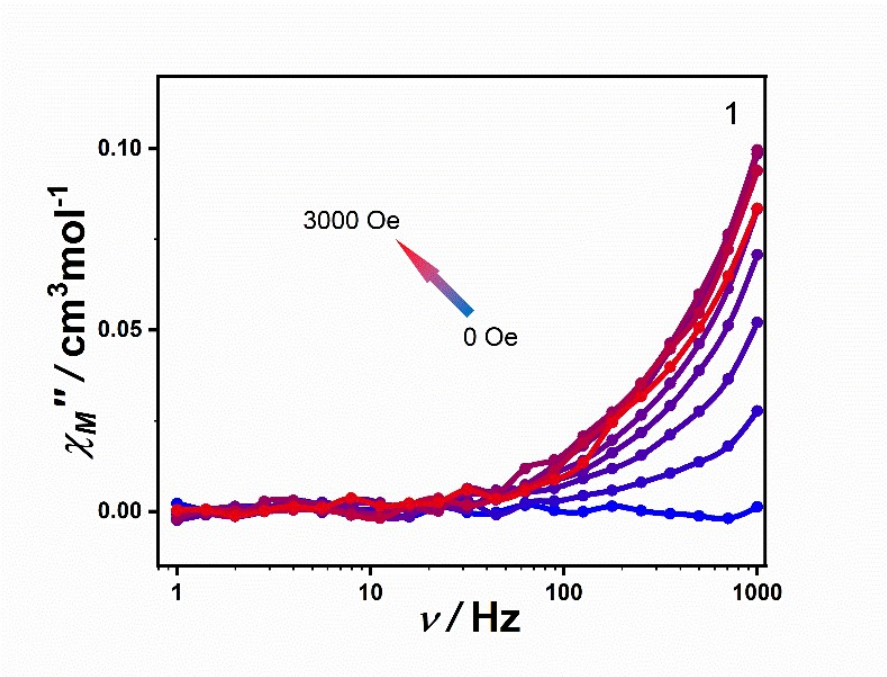
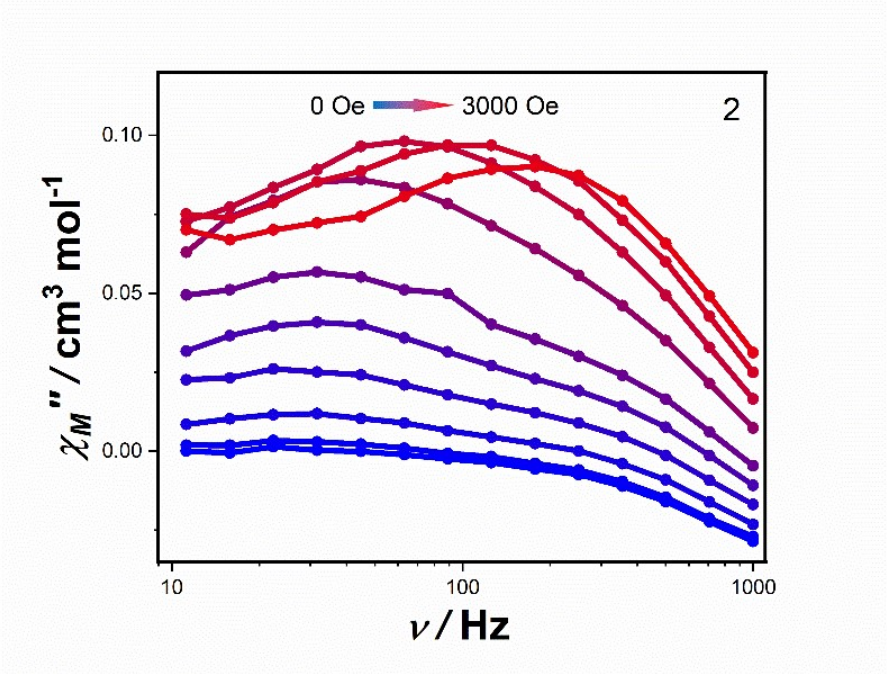


Fig. S7 XRD patterns for **2** (The red line is PXRD experimental pattern and the black line are calculated from single-crystal structure)



(a)



(b)

Fig. S8 Frequency dependence of out-of-phase ac susceptibility (χ_M'') under the different applied static fields from 0 to 0.3 T for **1** (a) and **2** (b) at 1.8 K. The solid lines are for eye guide.

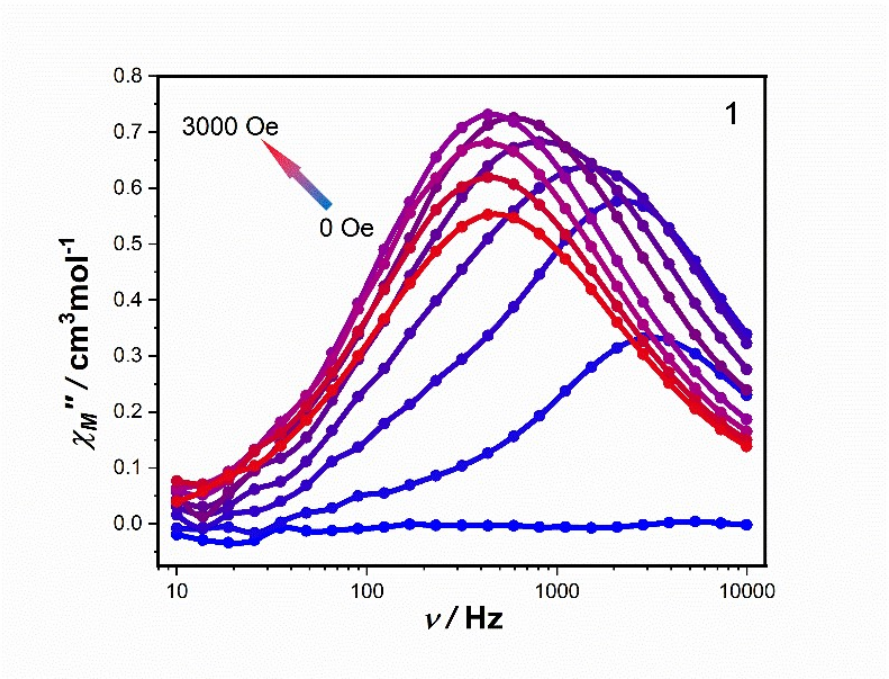


Fig. S9 Frequency dependence of out-of-phase ac susceptibility (χ_M'') under the different applied static fields from 0 to 0.3 T for **1** at 1.8 K. The frequency range is 10 - 10000 Hz and the solid lines are for eye guide.

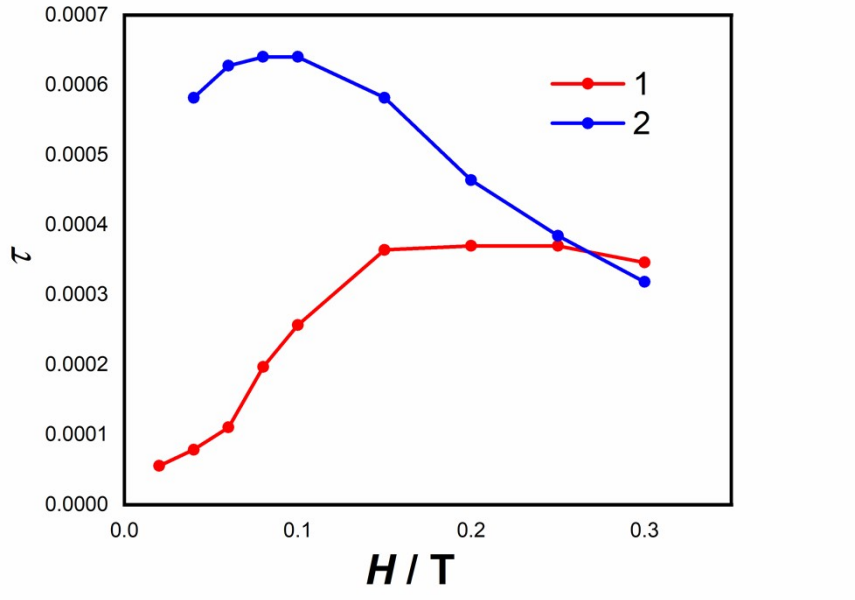
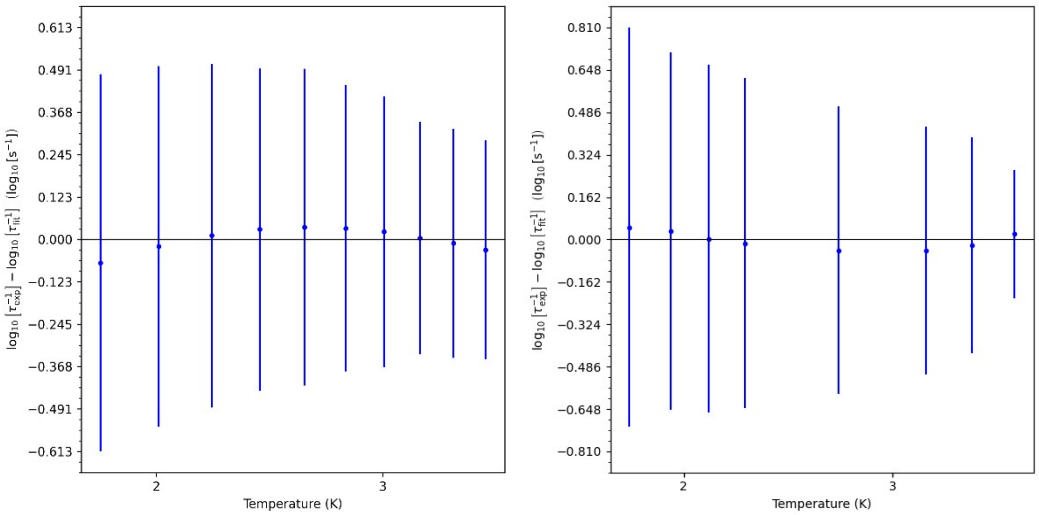


Fig. S10 The relaxation time τ of corresponding field for **1** and **2**.



(a) (b)

Fig. S11 The Raman residuals versus T for **1** (a) and **2** (b) fitted by CCfit2 program.

Table S6 Relaxation times τ (s) and α values for **1** and **2**.

				1				
T	τ	τ^{err}	χ_S	χ_S^{err}	χ_T	χ_T^{err}	α	α^{err}
1.8	3.1614×10^{-4}	5.11928×10^{-6}	0.54619	0.01175	2.49824	0.00925	0.17801	0.00815
2.0	1.86452×10^{-4}	3.35455×10^{-6}	0.54987	0.01401	2.37715	0.00895	0.1666	0.0092
2.2	1.18639×10^{-4}	2.17679×10^{-6}	0.55362	0.01481	2.23922	0.00729	0.15461	0.00927
2.4	8.04845×10^{-5}	1.51056×10^{-6}	0.56068	0.01528	2.1052	0.00561	0.13966	0.00916
2.6	5.75587×10^{-5}	9.30361×10^{-7}	0.55728	0.01319	1.99287	0.00449	0.13585	0.00778
2.8	4.41495×10^{-5}	8.90975×10^{-7}	0.57073	0.01647	1.8783	0.00448	0.11504	0.00956
3.0	3.35226×10^{-5}	7.84071×10^{-7}	0.57547	0.01794	1.78491	0.00371	0.105	0.00996
3.2	2.70145×10^{-5}	1.04017×10^{-6}	0.59297	0.02848	1.68953	0.00507	0.08024	0.01599
3.4	2.19474×10^{-5}	5.02922×10^{-7}	0.58788	0.01606	1.61802	0.00217	0.07854	0.00845
3.6	1.82317×10^{-5}	3.51846×10^{-7}	0.58723	0.01287	1.54881	0.0016	0.07214	0.00666
				2				
1.8	0.00479	3.59708×10^{-4}	0.56128	0.0027	0.73712	0.00653	0.28192	0.02876
1.95	0.0043	6.04246×10^{-4}	0.52109	0.00559	0.68839	0.0122	0.24417	0.06117
2.1	0.00404	2.26324×10^{-4}	0.48617	0.00232	0.64929	0.00477	0.2352	0.02543
2.25	0.00373	3.36182×10^{-4}	0.4568	0.00395	0.61478	0.00754	0.21933	0.04359
2.7	0.00289	3.07957×10^{-4}	0.38864	0.00528	0.5298	0.00796	0.1794	0.05932
3.2	0.00215	9.03009×10^{-5}	0.33325	0.00224	0.45765	0.00261	0.1431	0.02555
3.5	0.00175	6.26525×10^{-5}	0.30955	0.00195	0.42206	0.00191	0.11404	0.02281
3.8	0.00138	6.12936×10^{-5}	0.29365	0.00216	0.38957	0.00203	0.04484	0.03026

Notes and references

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