Isostructural M(II) Complexes (M = Mn, Fe, Co) with Field-Induced Slow Magnetic Relaxation for Mn and Co Complexes

Kaiji Uchida,*[,1] Goulven Cosquer,[1,2] Kenji Sugisaki,[3] Hideto Matsuoka,[3] Kazunobu Sato,[3] Brian K. Breedlove,[1] Masahiro Yamashita*[,1,2,4,5]

[1] Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba, Sendai 980-8578, Japan
[2] CREST, JST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
[3] Department of Chemistry and Molecular Materials Science, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan
[4] WPI Research Center, Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[5] School of Materials Science and Engineering, Nankai University, Tianjin 300350, China

Corresponding authors e-mail: masahiro.yamashita.c5@tohoku.ac.jp

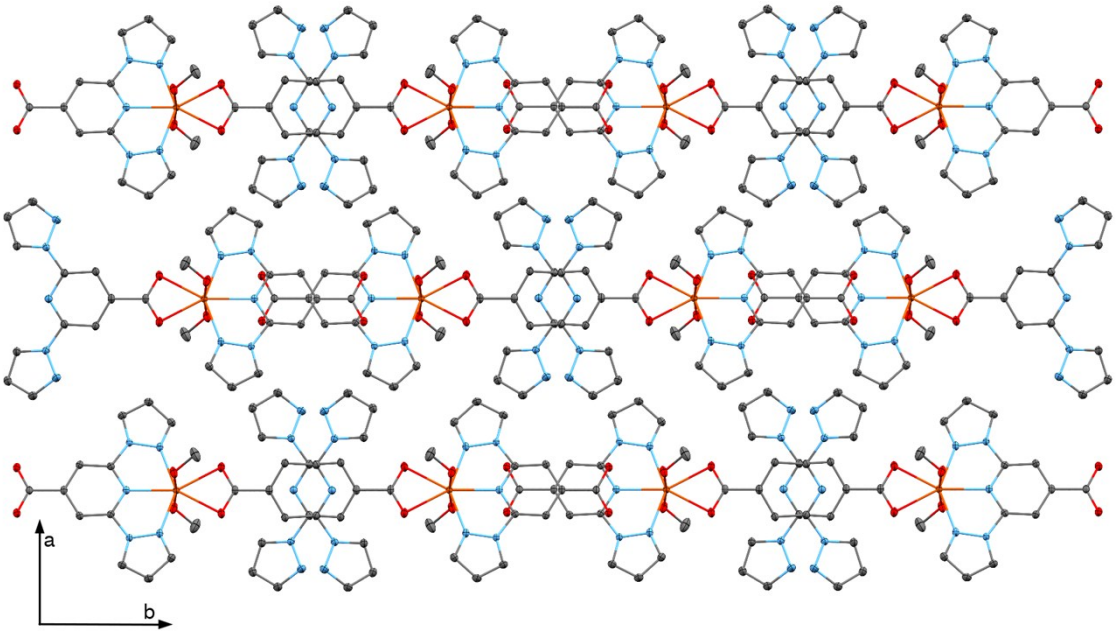


Figure S1 Arrangement of the molecules in **Fe** in the *ab* plan.

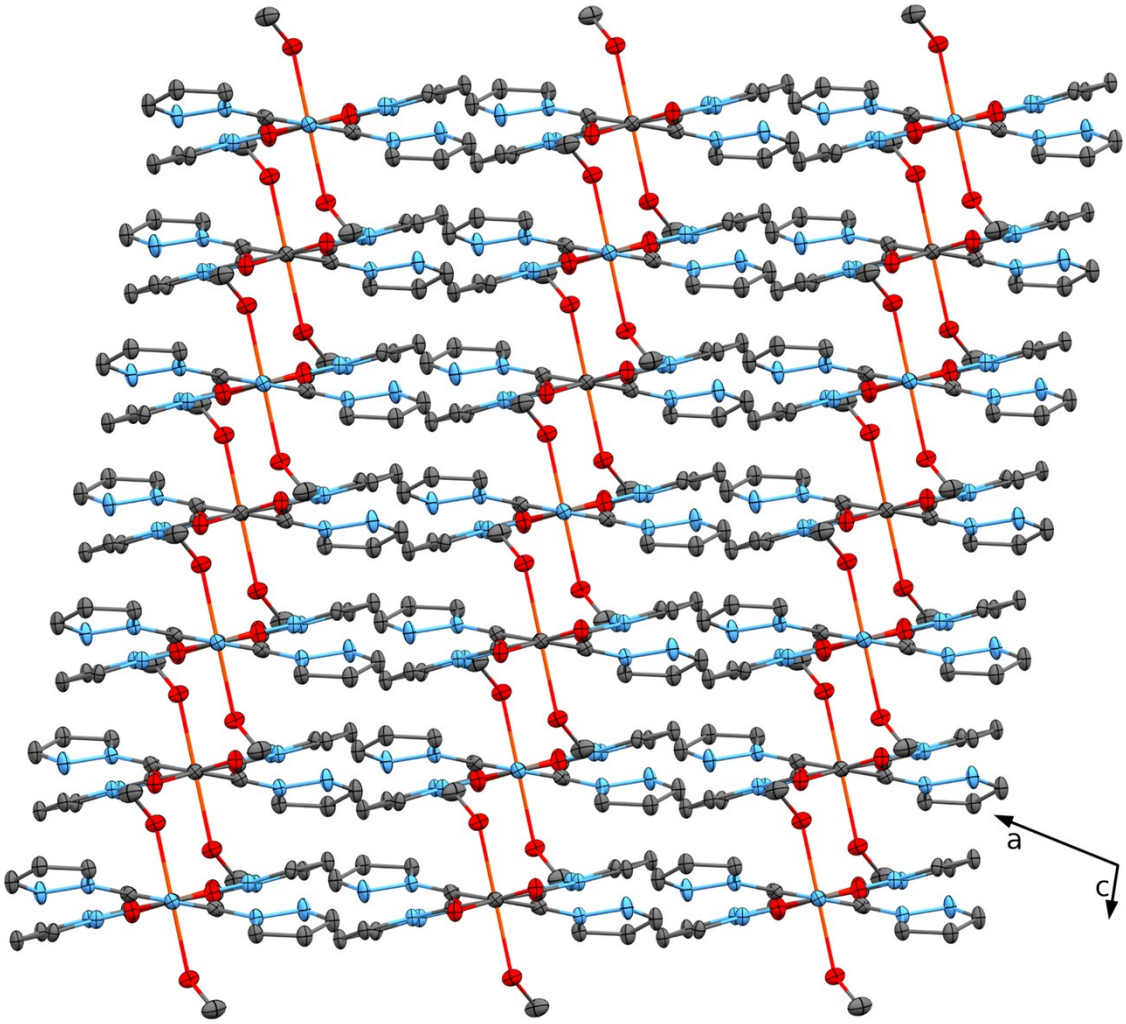


Figure S2 Arrangement of the molecule in **Fe** in the *ac* plan.

Table S1 Crystal parameters for the complexes.

	Mn	**Fe**	**Co**
Chemical Formula	$C_{26}H_{24}MnN_{10}O_6$	$C_{26}H_{24}FeN_{10}O_6$	$C_{26}H_{24}CoN_{10}O_6$
Crystal system	Monoclinic		
Space group	*C2/c*		
a (Å)	17.507(2)	17.4762(9)	17.5740(12)
b (Å)	21.925(3)	21.7676(11)	21.7514(13)
c (Å)	7.0181(9)	7.0315(4)	7.0063(5)
β (°)	103.348(12)	103.085(5)	103.552(7)
V (Å^3)	2621.1(6)	2605.4(2)	2603.7(3)
Z, *Z*′	4, 8		
*R*1 (%)	7.30	3.58	4.26
*wR*2 (%)	17.83	9.30	11.14

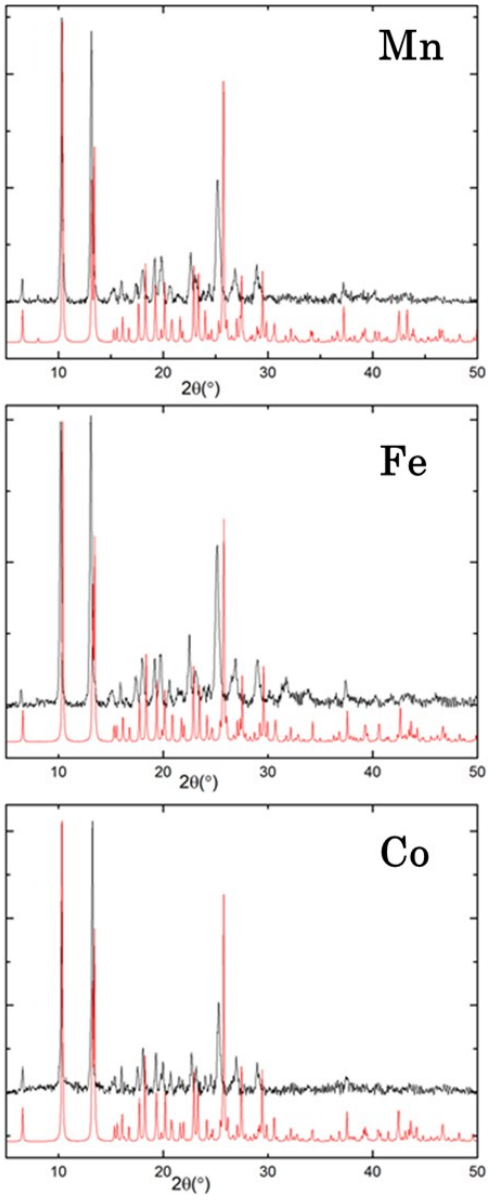


Figure S3 Powder X-ray diffraction diagram with experimental data (black) and simulated (red).

Table S2 Summary of the results from SHAPE 2.1 calculations.

Geometry	Symmetry	**Co**	**Fe**	**Mn**
Heptagon	D7h	33.099	33.167	33.417
Hexagonal pyramid	C6v	24.653	24.897	24.819
Pentagonal bipyramid	D5h	0.612	0.614	0.904
Capped octahedron	C3v	7.534	7.945	7.556
Capped trigonal prism	C2v	5.632	5.975	5.531
Johnson pentagonal bipyramid J13	D5h	3.485	3.405	3.587
Johnson elongated triangular pyramid J7	C3v	24.305	24.462	23.981

Table S3 Fitting parameters obtained from PHI software.

	Co	**Fe**	**Mn①**	**Mn②**
g_x	2.39	2.10	1.98	1.98
g_y				
g_z		1.98		
D (cm^{-1})	46.74	5.05	0.491	–0.423
E (cm^{-1})	0.651	1.45	4.47×10^{-4}	0
TIP (m^3mol^{-1})	0	7.69×10^{-10}	0	0

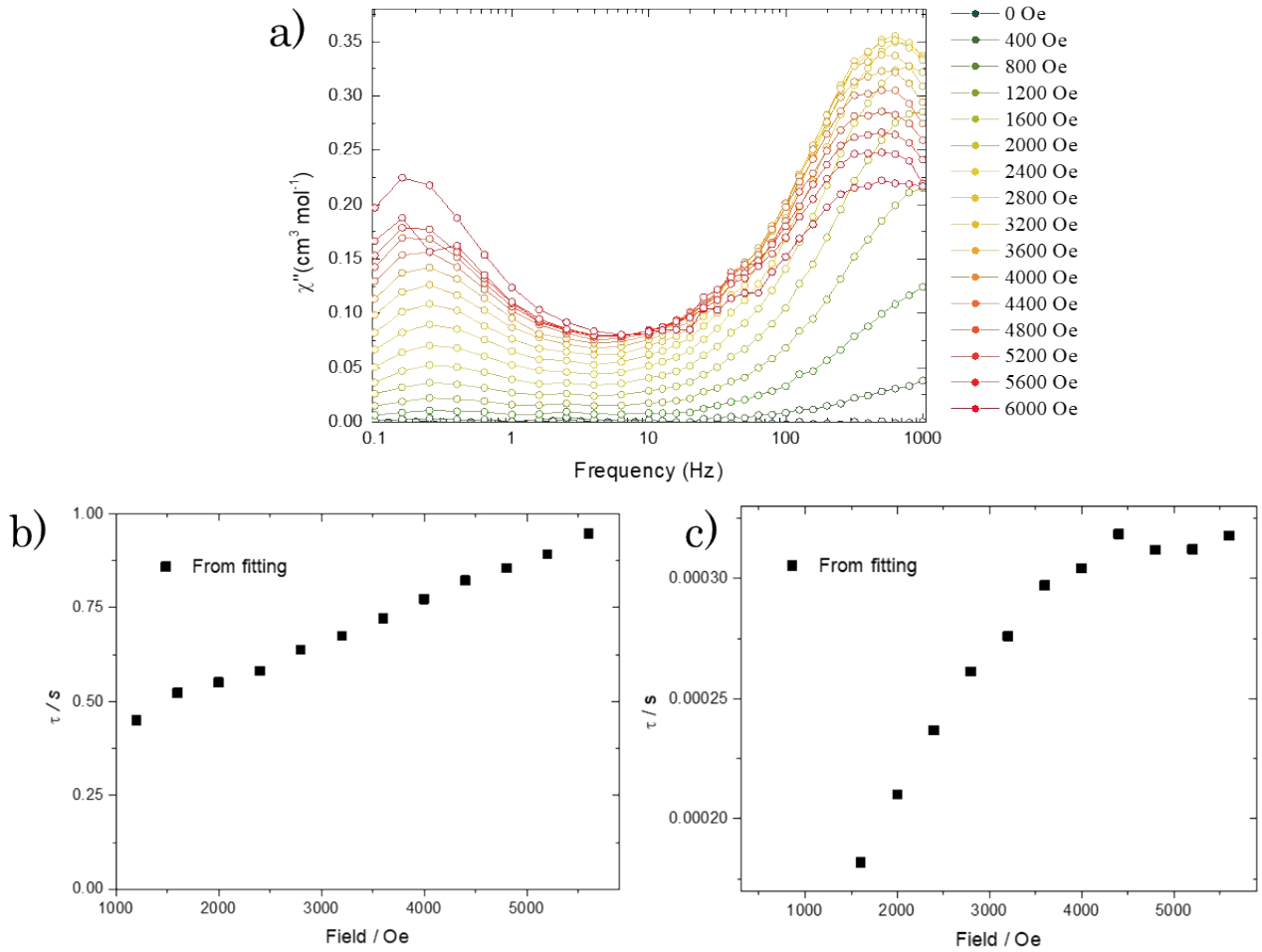


Figure S4 a) Field dependence of out-of-phase signal of **Mn** at 1.8 K.

b, c) Field dependence of relaxation time τ_{LF} and τ_{HF}.

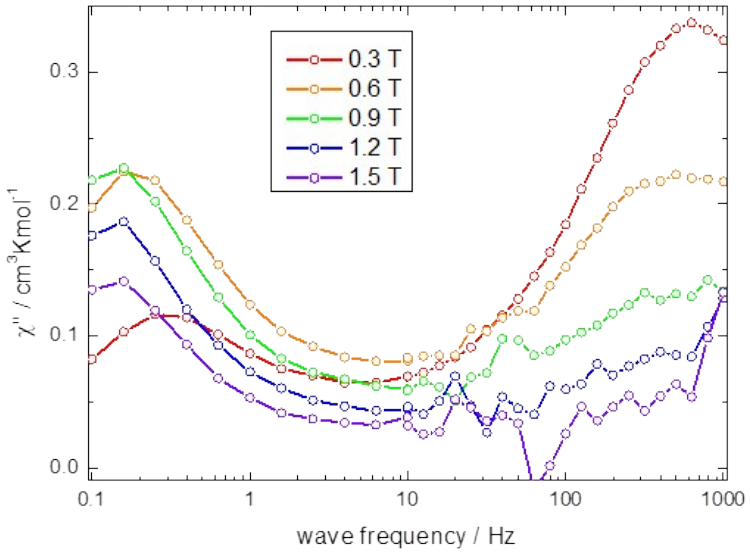


Figure S5 Field dependence of out-of-phase signal of **Mn** at 1.8 K under larger field.

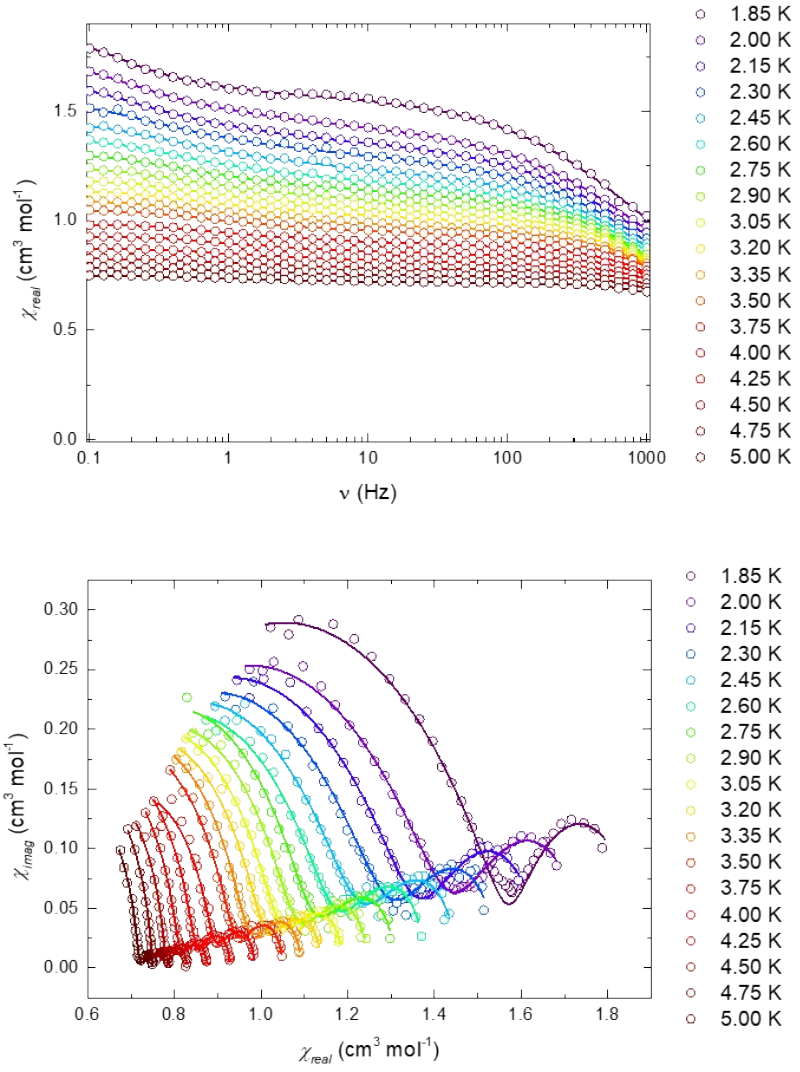


Figure S6 In-phase signal and Argand plot of **Mn** at 1.8 K under larger field.

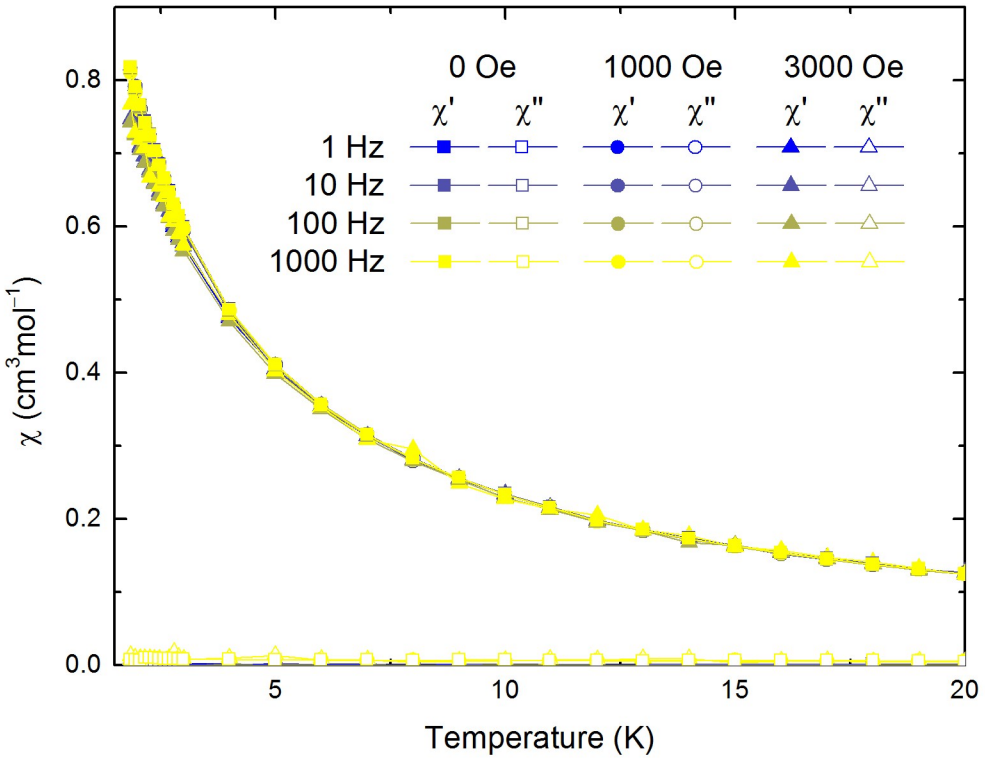
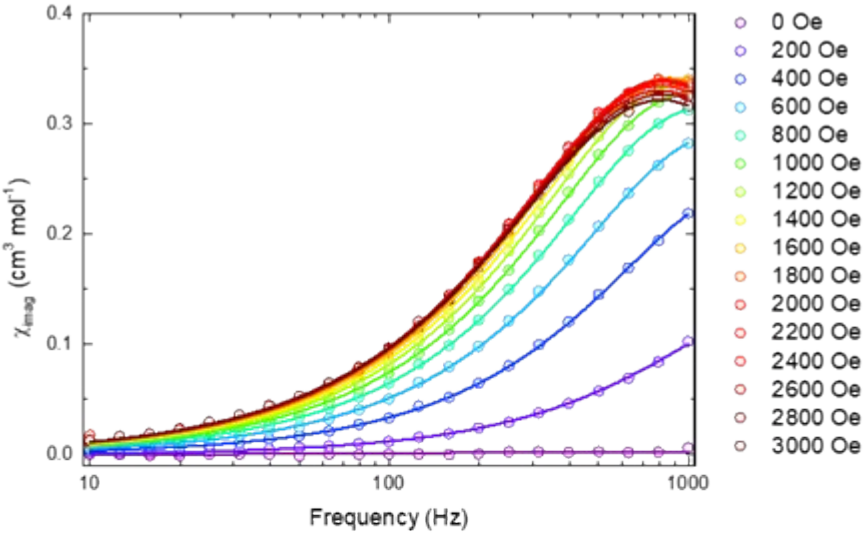


Figure S7 In-phase and out-of-phase signal of **Fe**.

a)


0.4
0.3
0.2
0.1
0.0
χ_{mag} (cm^3 mol^{-1})
10
100
1000
Frequency (Hz)
0 Oe
200 Oe
400 Oe
600 Oe
800 Oe
1000 Oe
1200 Oe
1400 Oe
1600 Oe
1800 Oe
2000 Oe
2200 Oe
2400 Oe
2600 Oe
2800 Oe
3000 Oe

b)

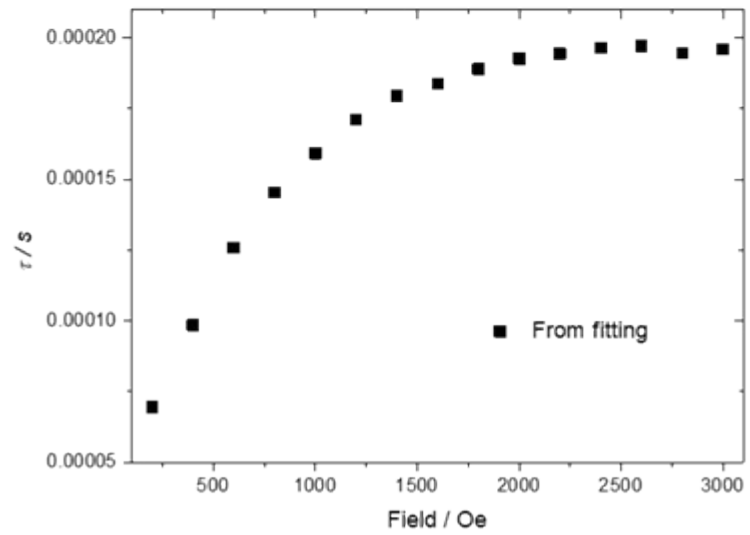

0.00020
0.00015
0.00010
0.00005
τ / s
500
1000
1500
2000
2500
3000
Field / Oe
From fitting

Figure S8 Field dependence of out-of-phase signal of **Co** at 1.8 K.

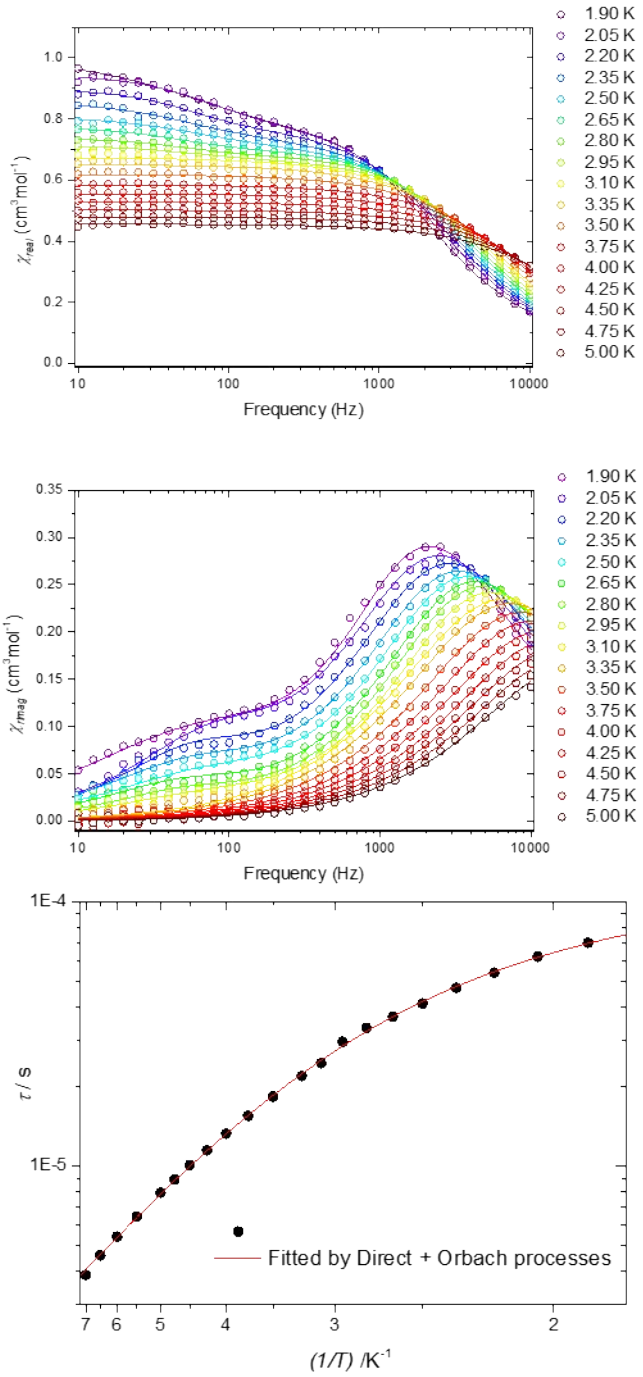


Figure S9 In-phase, out-of-phase signal and Arrhenius-like plot of **Co** in a 3000 Oe field.

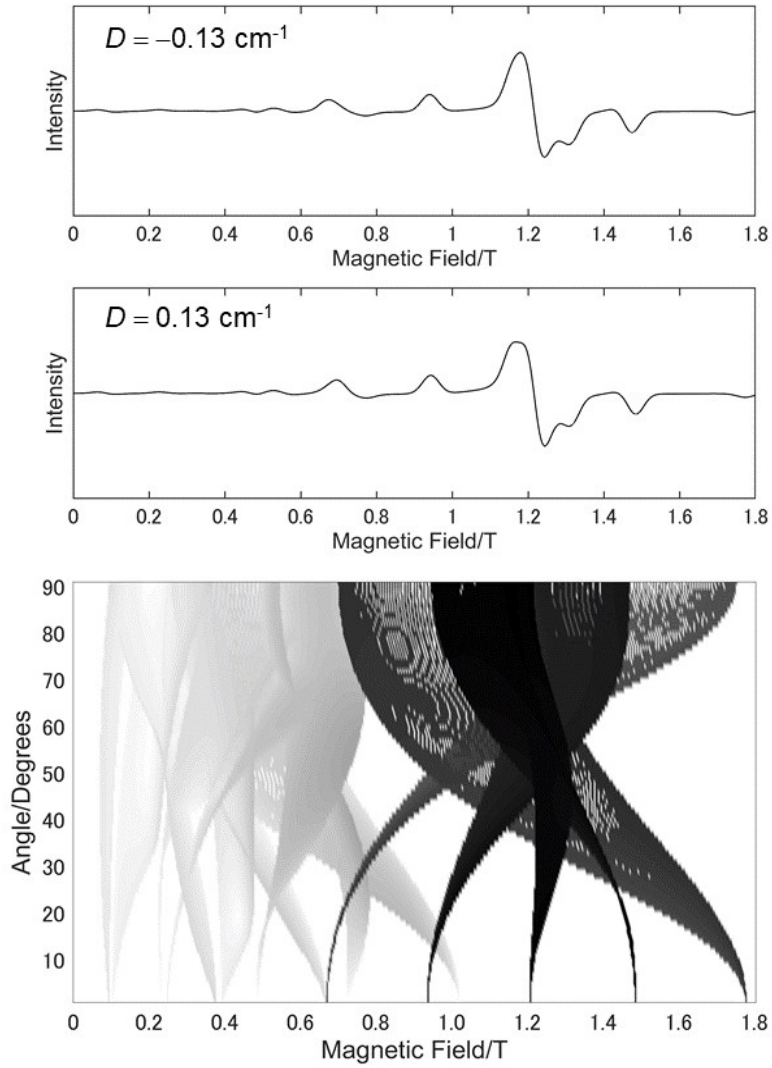


Figure S10 Simulated Q-band EPR spectra and angular dependence of the resonance fields with transition probabilities for the **Mn** complex with spin Hamiltonian parameters: $S = 5/2$, $g = (2.0, 2.0, 2.0)$, $D = \pm 0.13$ cm^{-1}, $|E/D|=0.3$.

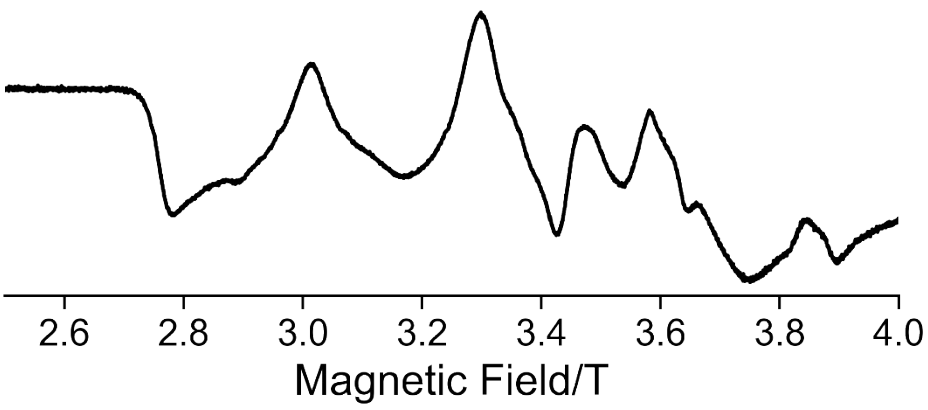


Figure S11 A W-band EPR spectrum of the Mn complex observed at 4K. MW frequency, 93.9468 GHz; MW power, 2 μW.

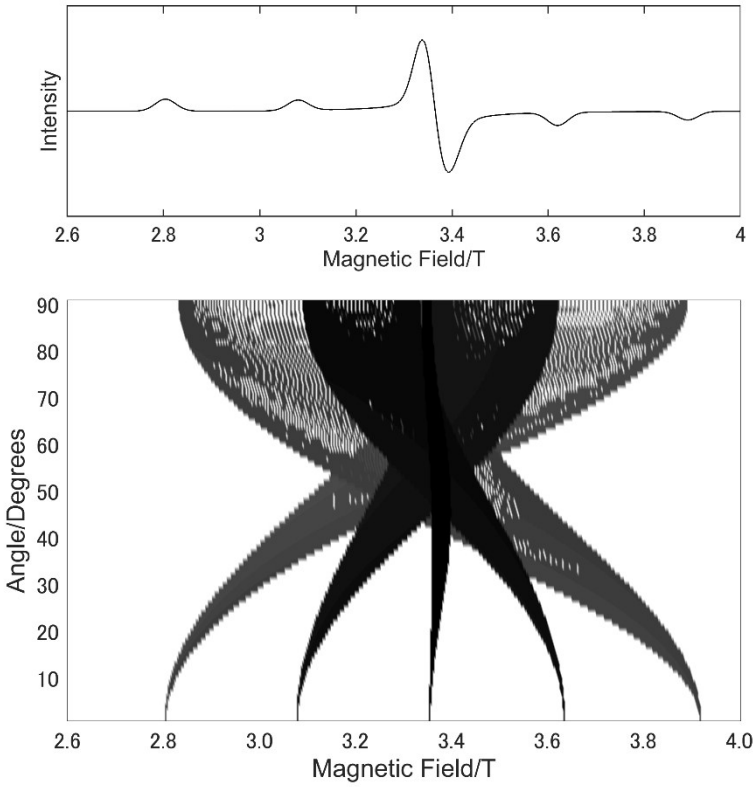


Figure S12 A simulated W-band EPR spectrum and angular dependence of the resonance fields with transition probabilities for the **Mn** complex with spin Hamiltonian parameters: $S = 5/2$, $g = (2.0, 2.0, 2.0)$, $D = -0.13$ cm^{-1}, $|E/D|=0.3$.