Supporting Information

Single Molecule Magnet Behavior in Bis-Oxamate One-dimensional Coordination Polymer: The Effect of Magnetic Dilution

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Table S1: Summary of data collection and crystal structure refinement for **1** and **2a**.

	1	**2a**
Formula	$C_{16}H_{18}N_2O_{12}S_1Mn_1$	$C_{16}H_{20}N_2O_{13}S_1Co_{0.87}Cu_{0.13}$
Fw (g mol^{-1})	517.32	539.93
T (K)	140	100
λ (Å)	1.54184	0.82654
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*
a (Å)	20.230(2)	19.817(2)
b (Å)	5.097(1)	5.062(1)
c (Å)	21.536(2)	21.336(3)
α (º)	90	90
β (º)	98.32	98.62(2)
γ (º)	90	90
Volume (Å^3)	2197.1(3)	2116.1(4)
Z	4	4
ρ_{calc} (Mg m^{-3})	1.564	1.695
μ (mm^{-1})	6.370	1.518
F(000)	1060	1109
θ range (Deg.)	4.149-66.218	2.246-28.703
Index ranges	-23<=h<=23, -5<=k<=5, -25<=l<=25	-22<=h<=22, -5<=k<=5, -24<=l<=24
Data collected/ Independent reflections	2805/2805	2295/2295
R_{int}	0.078	0.102
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2805/17/174	2295/50/119
GOF on F^2	1.032	1.030
R_1;wR_2 [I>2σ(I)]	0.0660, 0.1763	0.0948, 0.2427
R_1;wR_2 (all)	0.0899, 0.1961	0.1457, 0.2727
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e·Å^{-3})	0.470, -0.413	1.054, -0.801

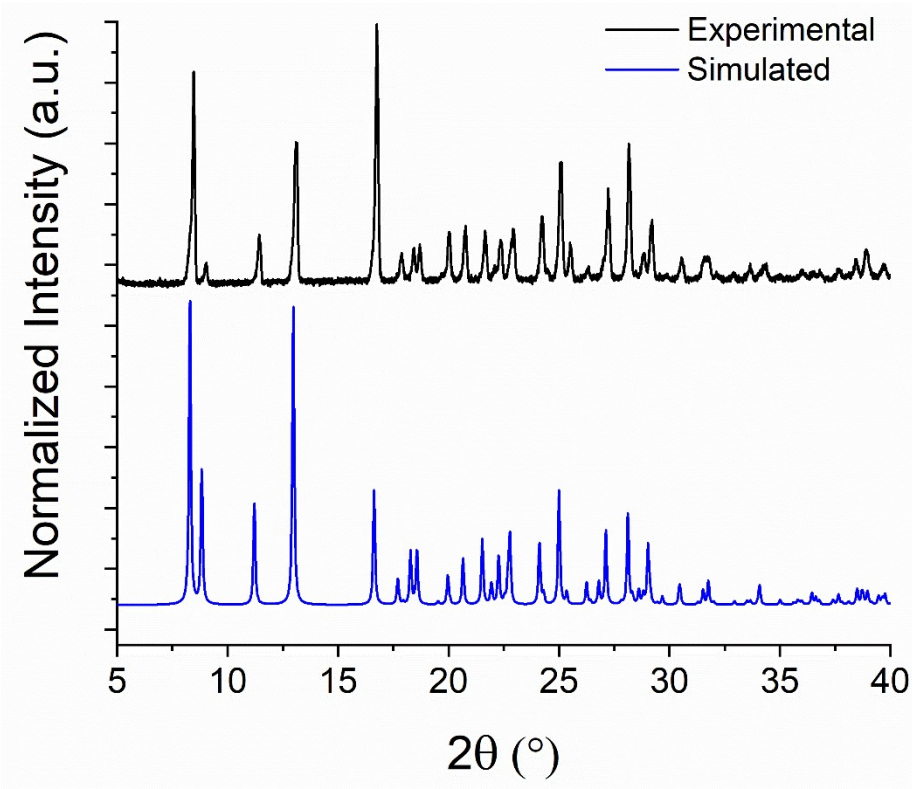


Fig. S1: Comparison between experimental and simulated diffractograms of **1**.

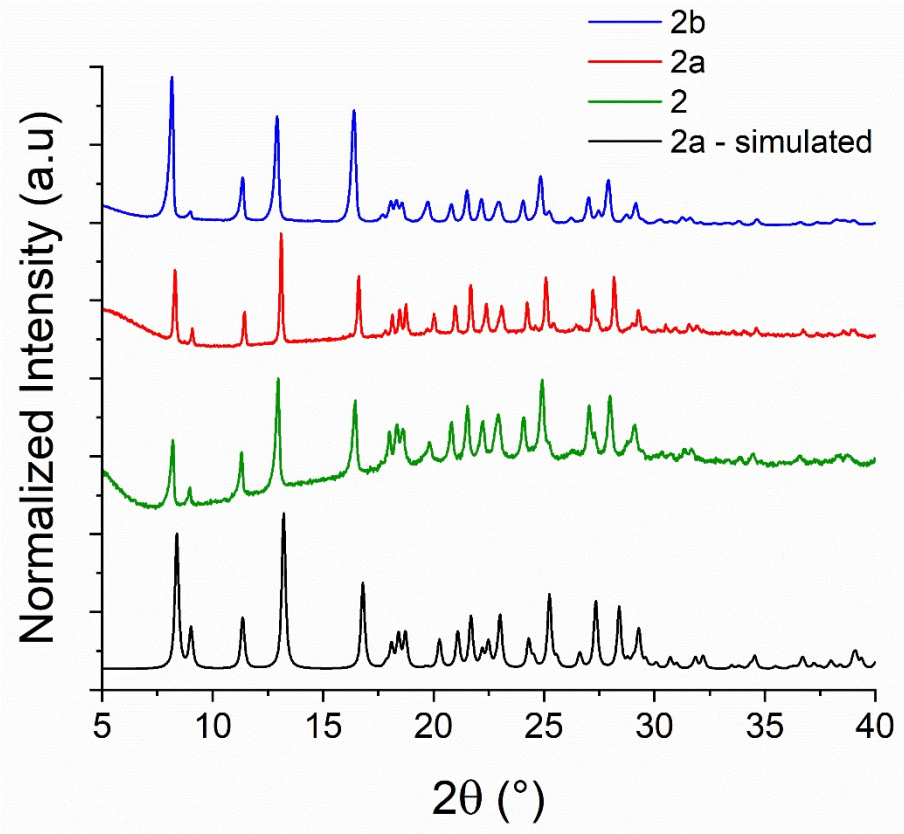


Fig. S2: Comparison between experimental and simulated diffractograms of **2**, **2a** and **2b.**

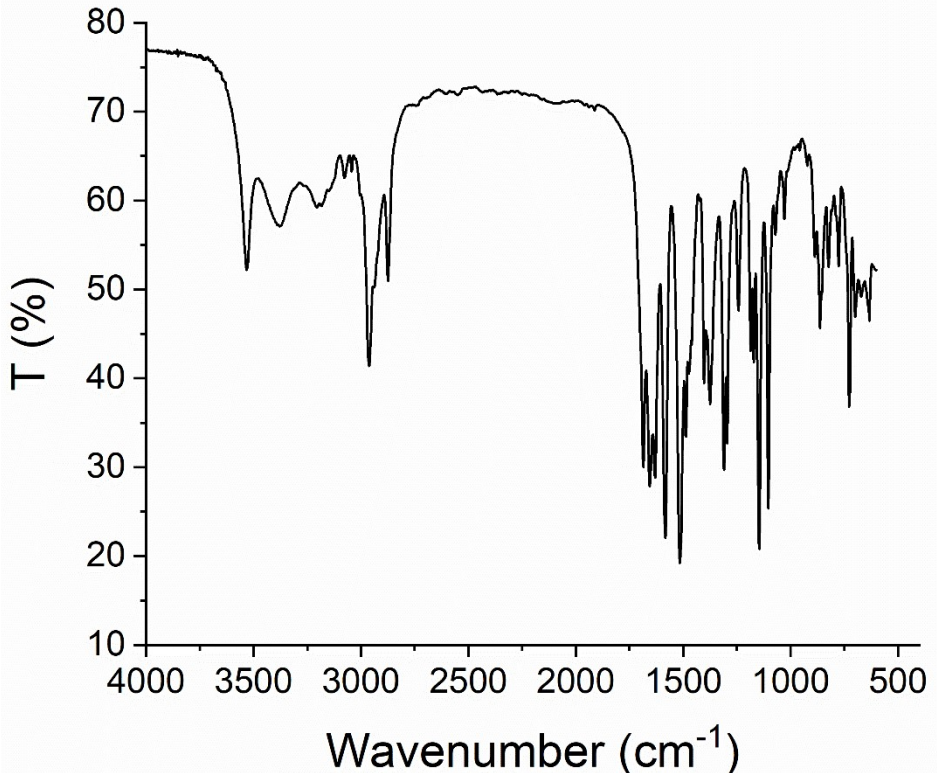


Fig. S3: Fourier Transform Infrared spectrum of compound $(NBu_4)_2L$.

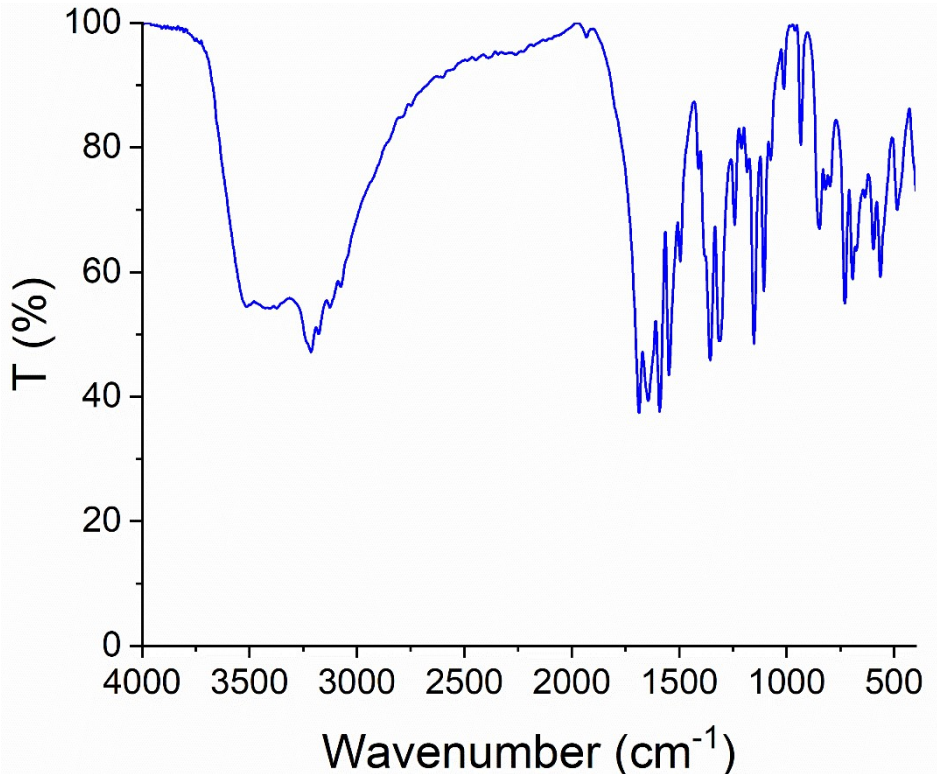


Fig. S4: Fourier Transform Infrared spectrum of compound **1**.

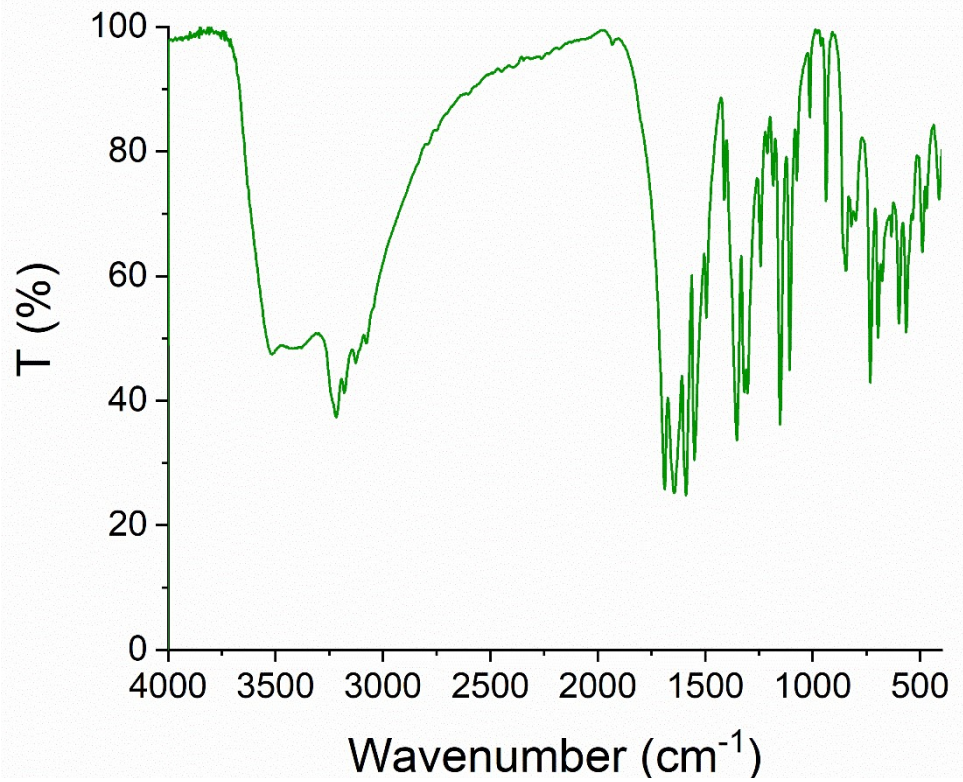


Fig. S5: Fourier Transform Infrared spectrum of compound **2**.

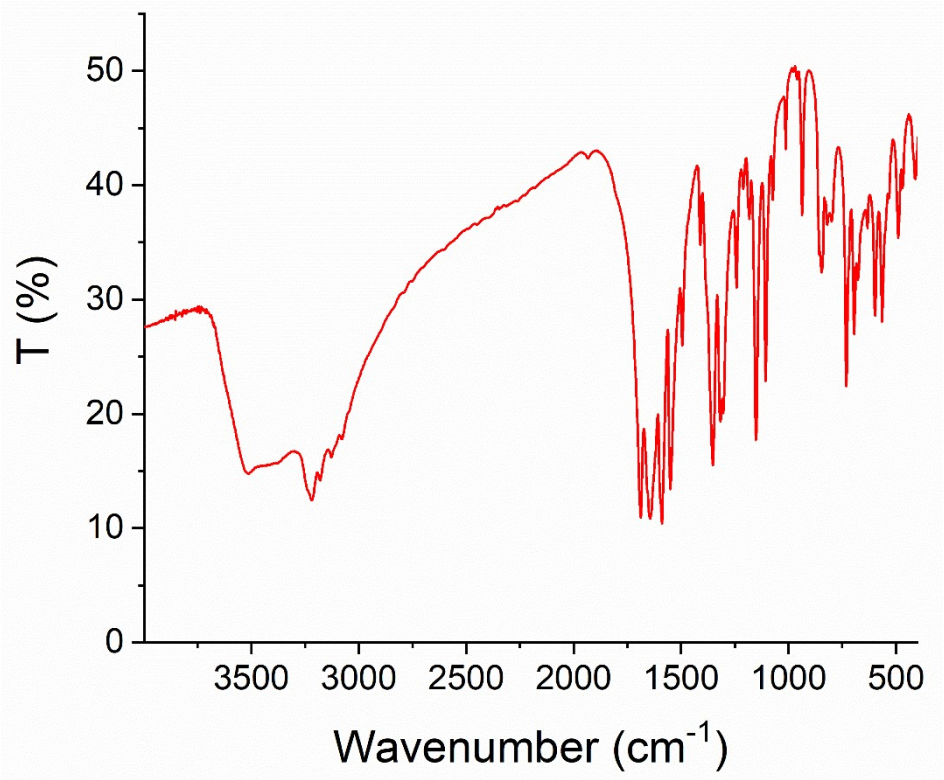


Fig. S6: Fourier Transform Infrared spectrum of compound **2a**.

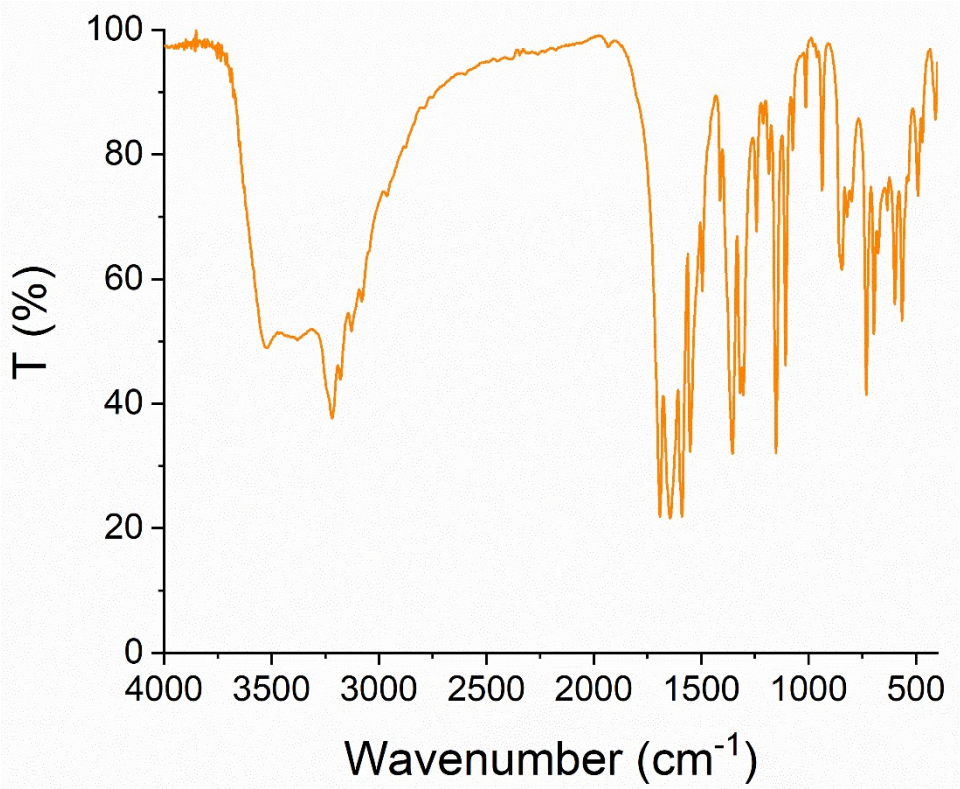


Fig. S7: Fourier Transform Infrared spectrum of compound **2b**.

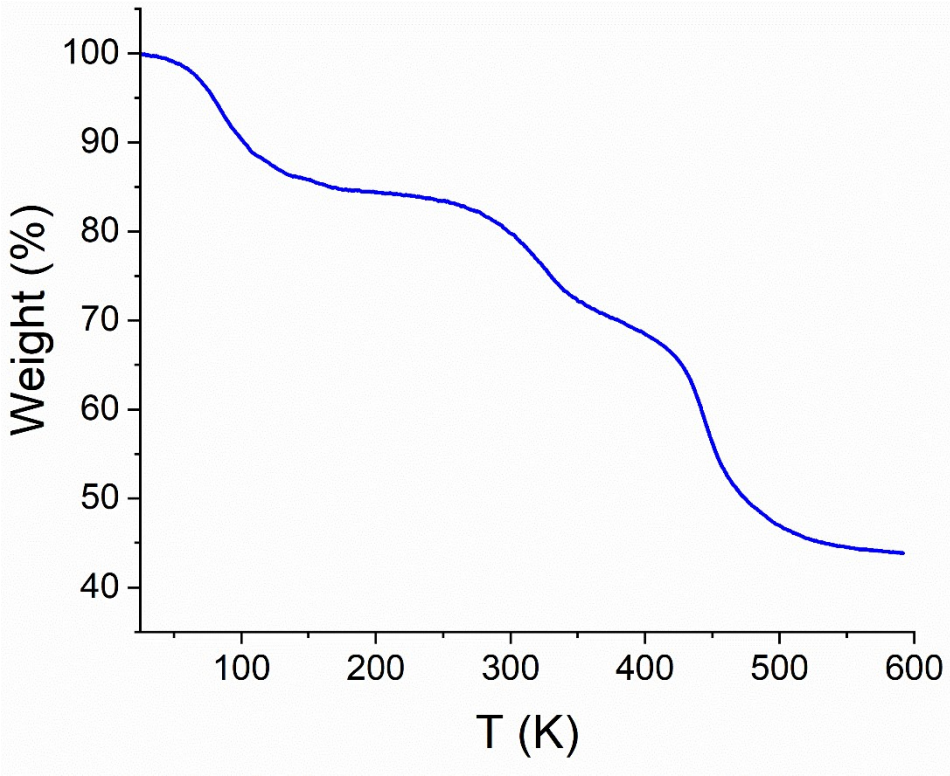


Fig. S8: Thermogravimetric analysis of **1**.

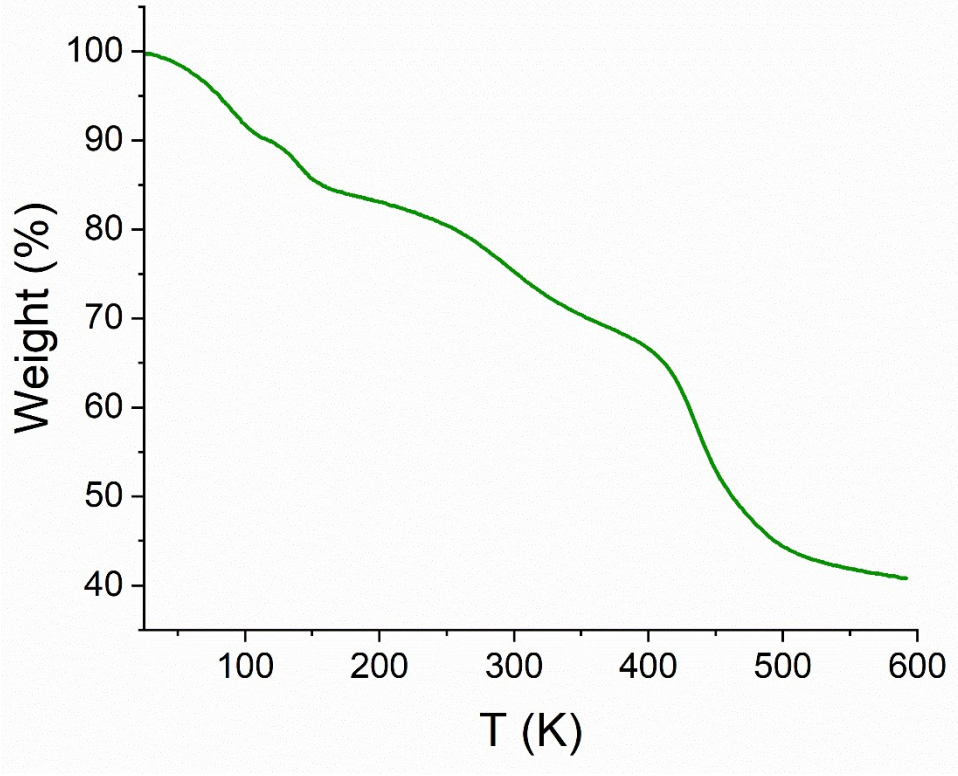


Fig. S9: Thermogravimetric analysis of **2**.

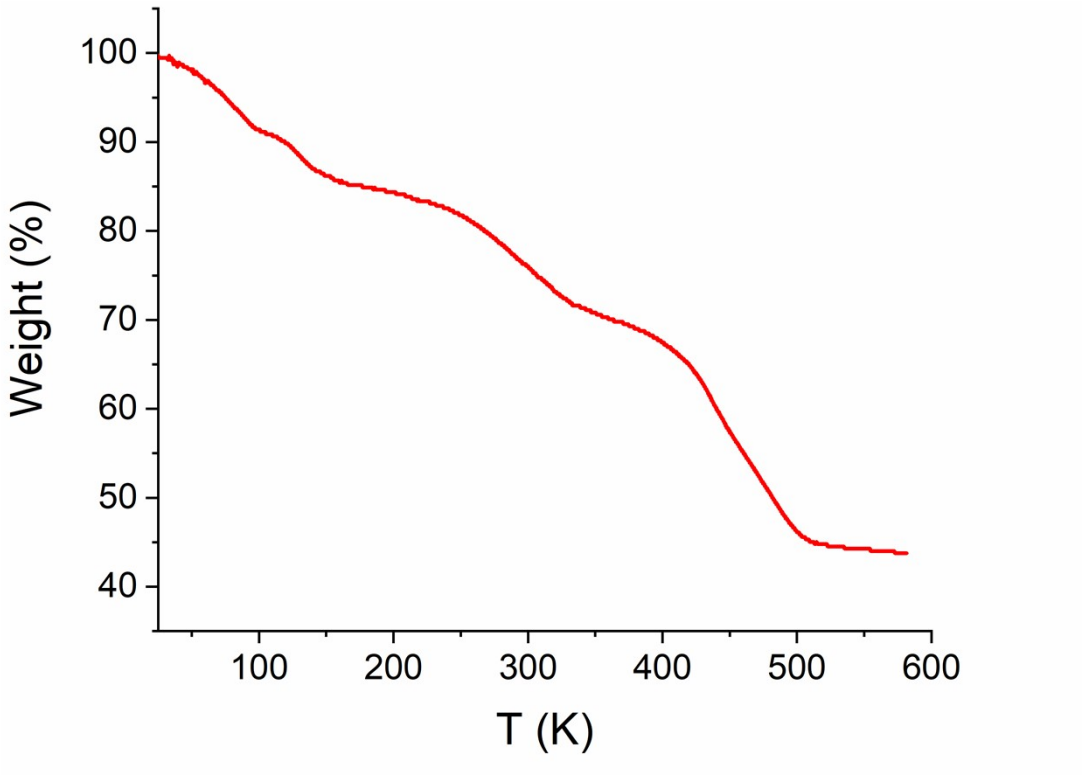


Fig. S10: Thermogravimetric analysis of **2a**.

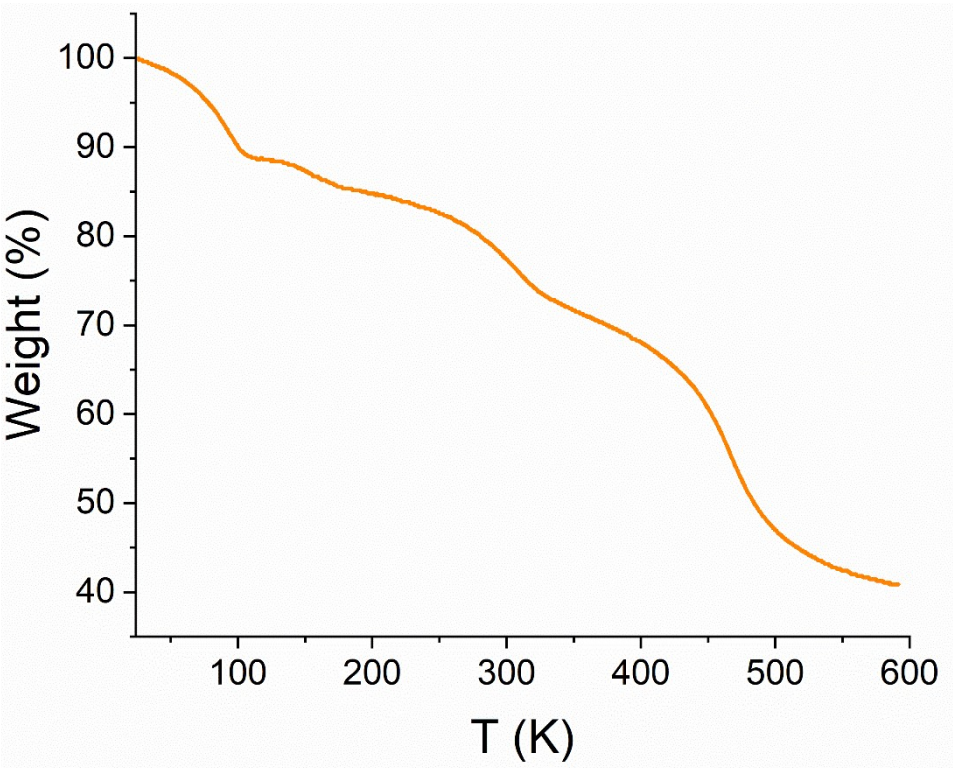


Fig. S11: Thermogravimetric analysis of **2b**.

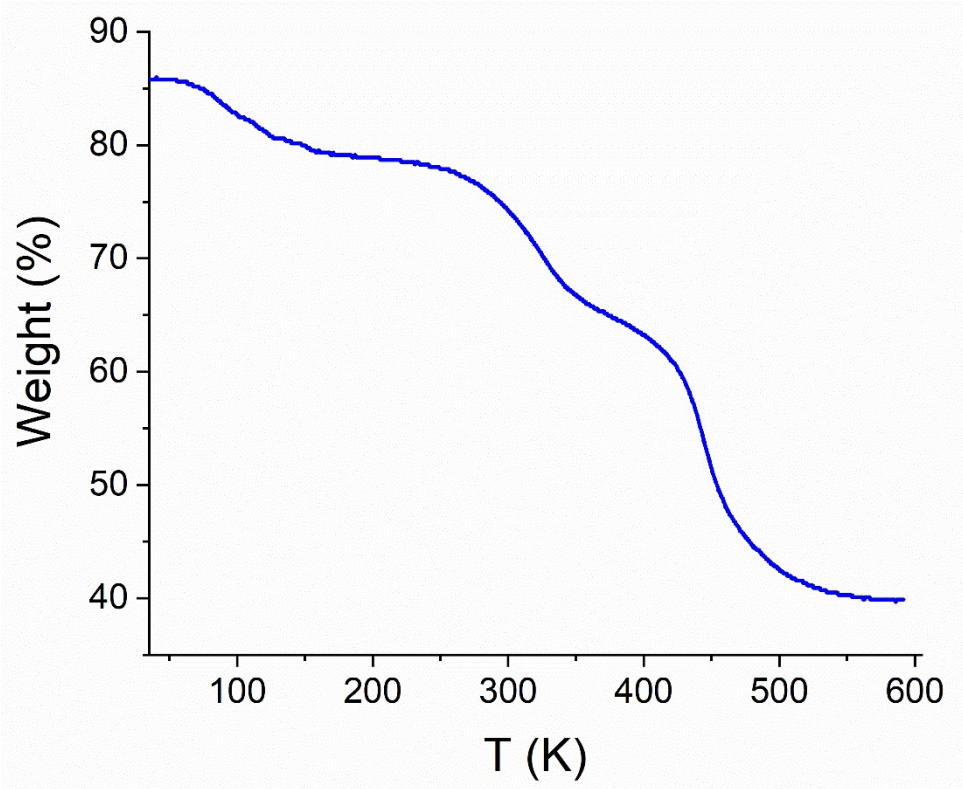


Fig. S12: Thermogravimetric analysis of **1** after keeping the sample at 305 K (32°C) for 2 hours.

Table S2: Selected bond lengths and bond angles for **2a**.

Bond Lengths (Å)			
Co1-O1		2.136(7)	
Co1-O2		2.035(8)	
Co1-O3		2.106(9)	
Bond Angles (º)			
O2-Co1-O1	80.6(3)	O2[a]-Co1-O1	99.4(3)
O2-Co1-O3	91.8(3)	O3[a]-Co1-O1	86.1(3)
O2-Co1-O1[a]	99.4(3)	O2[a]-Co1-O1[a]	80.6(3)
O2-Co1-O3[a]	88.2(3)	O3[a]-Co1-O1[a]	93.9(3)
O3-Co1-O1	93.9(3)	O3-Co1-O3[a]	180.0
O3-Co1-O1[a]	86.1(3)	O1-Co1-O1[a]	180.0(3)
O2[a]-Co1-O3	88.2(3)	O2[a]-Co1-O2	180.0
O2[a]-Co1-O3[a]	91.8(3)		

[a] symmetry operation to generate equivalent atoms: -x+1/2,-y+3/2,-z+1

Table S3: Results of the analysis using program SHAPE.

Compound	Atom	**OC-6**	HP-6	PPY-6	TPR-6	JPPY-6
1	Mn1	**1.020**	28.312	28.045	15.293	30.947
2a	Co1	**0.572**	29.116	28.179	15.470	31.155

OC-6 Octahedron, HP-6 Hexagon, PPY-6 Pentagonal pyramid, TPR-6 Trigonal prism, JPPY-6 Johnson pentagonal pyramid J2

Table S4: Distortion parameters calculated using the program OCTADIST.

Compound	Atom	**ζ(Å)**	**Σ(°)**	**Θ(°)**	V (Å^3)
1	Mn1	0.165	79.48	244.97	13.2
2a	Co1	0.231	60.14	172.07	12.0

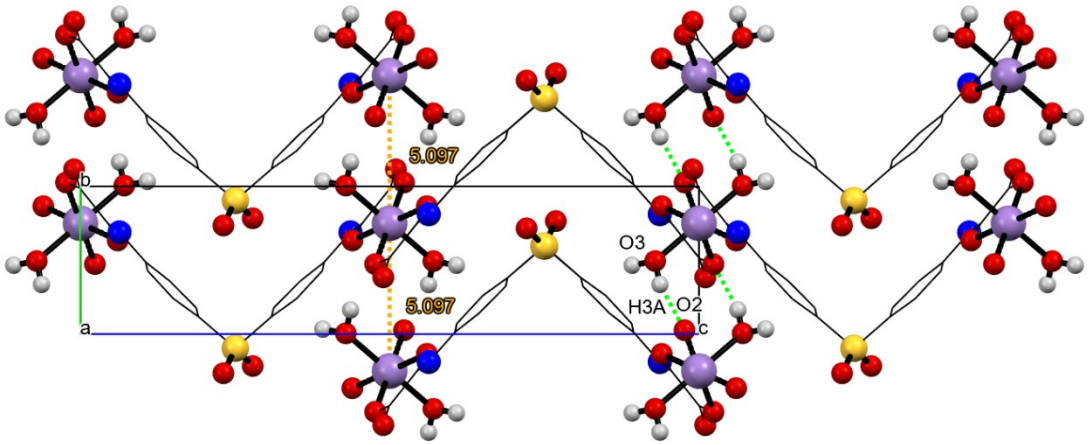


Fig. S13: Crystal packing viewed along the crystallographic direction *a* for **1**. Hydrogen bonds are represented as dashed green lines and orange dashed green lines represent the shortest Mn···Mn interchain distance.

Table S5: Hydrogen bond parameters for **1**.

D-H	d(D-H) (Å)	d(H···A) (Å)	<DHA (°)	d(D···A) (Å)	A	Symmetry Operation[b]
N1-H1	0.90(5)	1.99(5)	171(6)	2.885(7)	O4[b]	-x+1, -y+2, -z+1
O7A-H7AA	0.85	2.07	166	2.91(2)	O6[b]	x-1/2, y+3/2, z
O7A-H7AA	0.85	1.68	168	2.52(2)	O5[b]	-x+1/2, y+3/2, -z+1/2
O7A-H7AB	0.85	2.19	146	2.93(3)	O7B[b]	-x+1/2, y+1/2, -z+1/2
O3-H3A	0.86(4)	1.84(4)	164(4)	2.670(7)	O2[b]	-x+1/2, -y+5/2, -z +1
O3-H3B	0.89(5)	1.97(4)	148(7)	2.76(1)	O7A[b]	x, y, z

Table S6: Hydrogen bond parameters for **2a**.

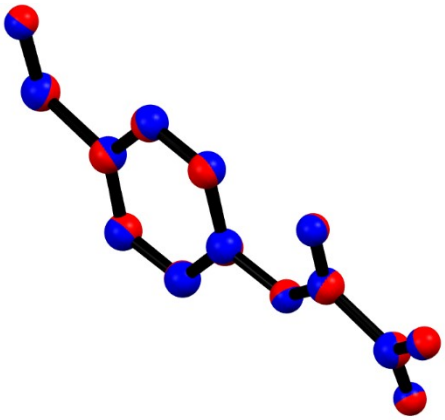
D-H	d(D-H) (Å)	d(H···A) (Å)	<DHA (°)	d(D···A) (Å)	A	Symmetry Operation[b]
N1-H1	0.87(5)	2.04(5)	161(5)	2.87(1)	O4[b]	-x+1, -y+2, -z+1
O7A-H7AB	0.89	1.83	137	2.56(2)	O6	-x+1, y, -z+1/2
O7A-H7AB	0.89	2.27	149	3.07(2)	O5	x,y,z
O7A-H7AA	0.91	1.78	141	2.55(3)	O7B	-x+1/2, y-1/2, -z+1/2
O3-H3A	0.86	1.82	163	2.65(1)	O2[b]	-x+1/2, -y+5/2, -z+1
O3-H3B	0.85	2.21	129	2.82(2)	O7A[b]	-x+1/2, y+3/2, -z+1/2

Table S7: Results from the isostructurality analysis calculated using the programs ISOS and Mercury.

	Cell Similarity Index (π)	Isostructurality Index (I(s))	RMSD
Whole structure[a,b]	0.0176	74.6%	-
Chain[a,b]	0.0176	75.2%	0.0517
Coordination sphere[a,b]	0.0176	77.8%	0.0732
Ligand[a,b]	0.0176	75.2%	0.0233

[a]Lattice water molecules were not considered. [b]Only asymmetric unit was used in the analysis.

a)



b)

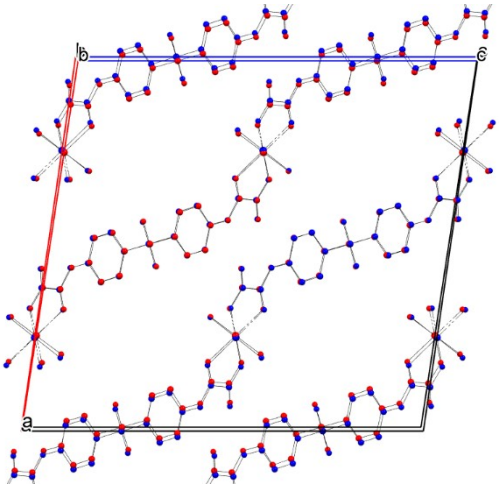


Fig. S14: Structure overlay for **1** and **2a** emphasizing the organic ligand (a) and crystal packing along the crystallographic direction *b* (b).

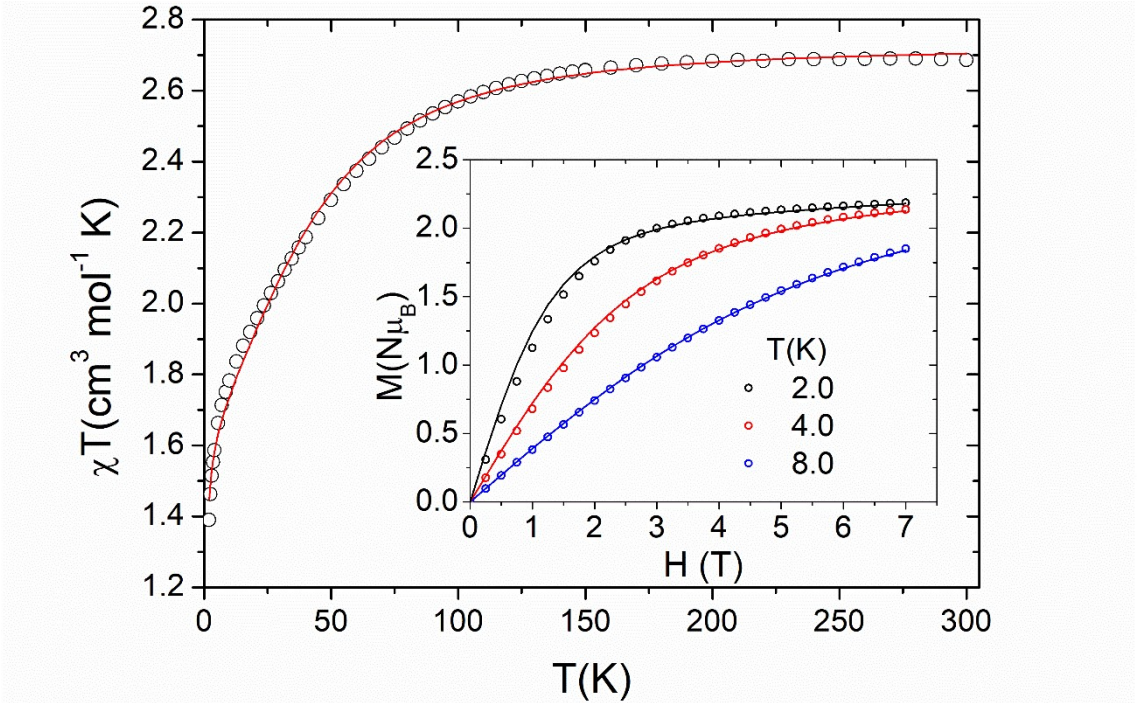


Fig. S15: Temperature dependence of χT for **2**. The lines represent the best fit curves using Eq. 3 with the experimental parameters mentioned in Table 2 for D>0. Inset: Field dependence of magnetization.

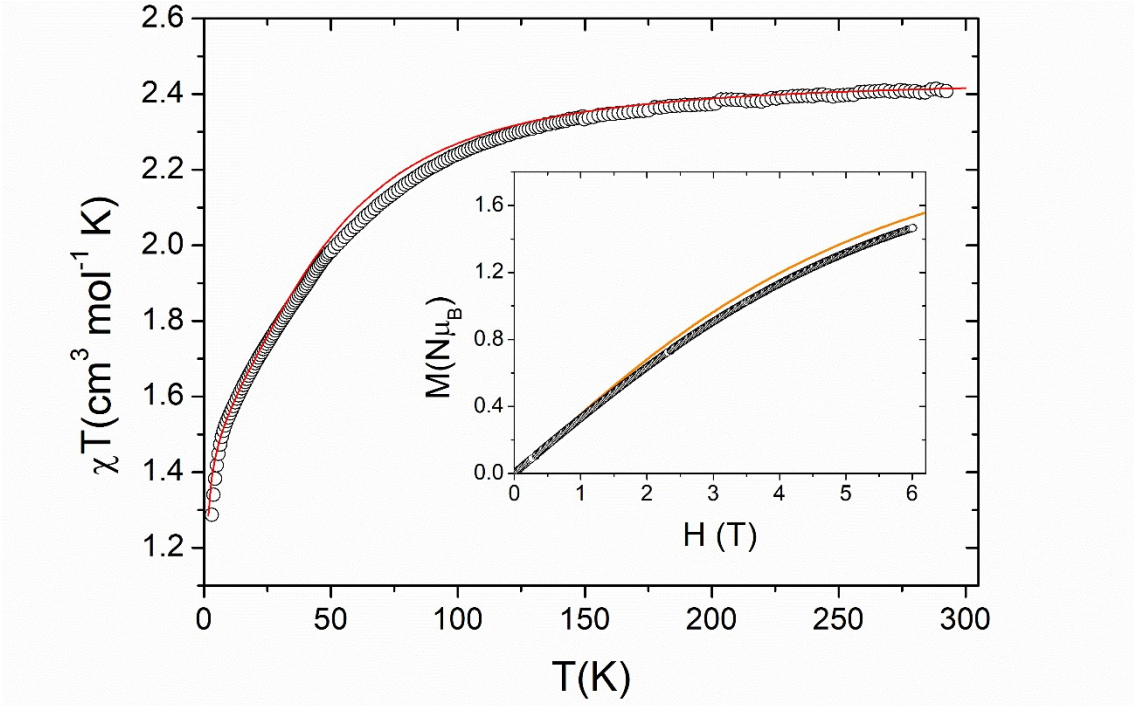


Fig. S16: Temperature dependence of χT for **2a**. The lines represent the simulation using Eq. 3 with the experimental parameters mentioned in Table 2 for D>0 plus a contribution of paramagnetic copper(II) ion with average g value equals to 2.15. Inset: Field dependence of magnetization at 8.0K.

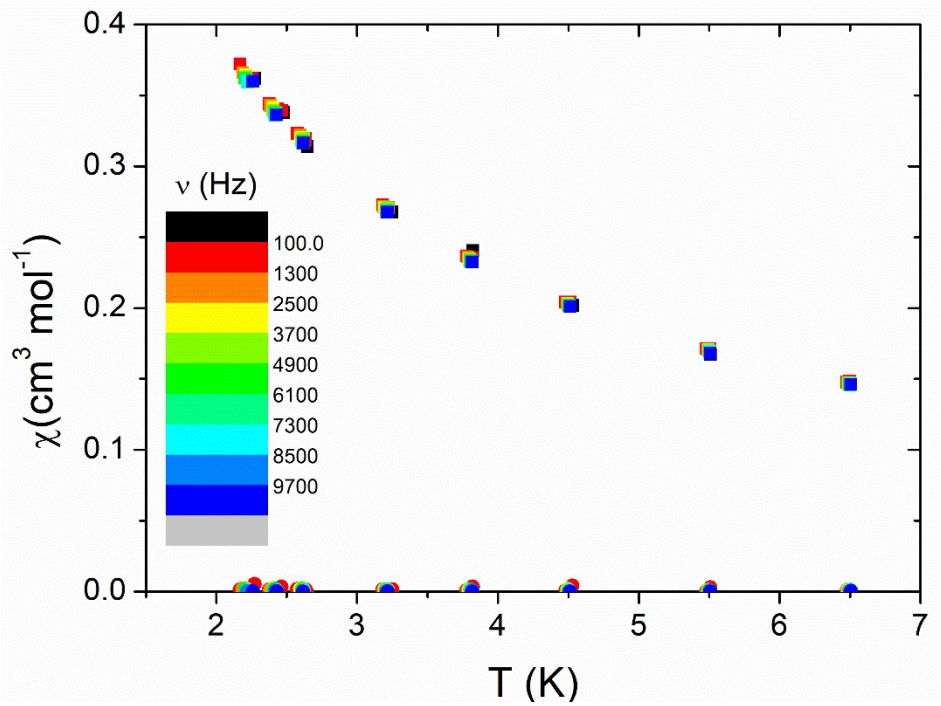


Fig. S17: Temperature dependence of in-phase (square) and out-of-phase (circles) magnetic susceptibilities at zero dc field for **2** at different frequencies**.**

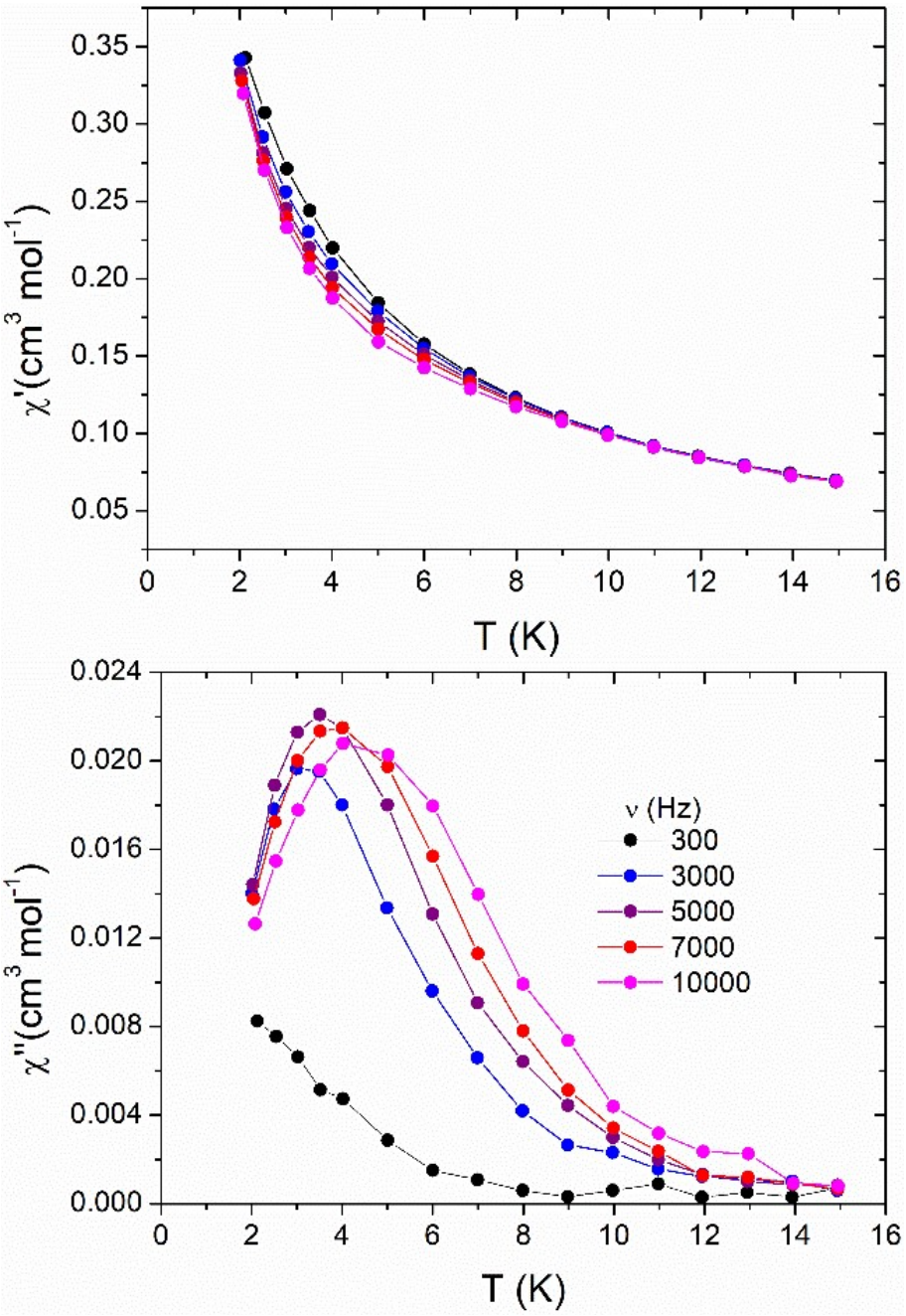


Fig. S18: Temperature dependence of χ' (up) and χ''(bottom) under applied dc field of 0.2 T for **2** at selected frequencies.

Table S8: Relaxation fitting parameters for **2b** using Eq. S1.

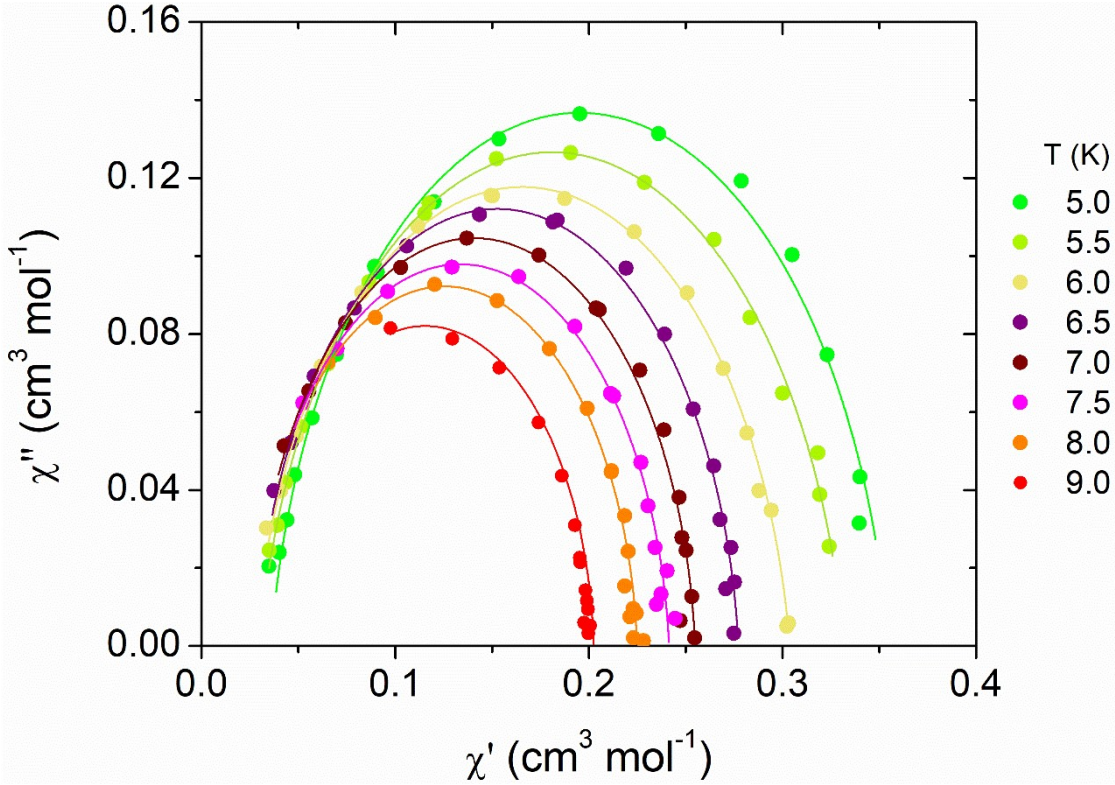
T (K)	χ_S (cm^3 mol^{-1})	$\chi_T - \chi_S$ (cm^3 mol^{-1})	α	τ (s)
2.0	8.14 x 10^{-2}	0.799	0.206	5.21 x 10^{-3}
2.2	7.86 x 10^{-2}	0.697	0.188	4.00 x 10^{-3}
2.4	6.60 x 10^{-2}	0.763	0.178	3.76 x 10^{-3}
2.6	6.33 x 10^{-2}	0.616	0.190	3.16 x 10^{-3}
2.8	6.33 x 10^{-2}	0.557	0.156	2.58 x 10^{-3}
3.0	5.50 x 10^{-2}	0.559	0.192	2.50 x 10^{-3}
3.2	5.10 x 10^{-2}	0.508	0.183	2.05 x 10^{-3}
3.4	4.77 x 10^{-2}	0.517	0.197	2.02 x 10^{-3}
3.6	4.55 x 10^{-2}	0.466	0.180	1.61 x 10^{-3}
3.8	4.03 x 10^{-2}	0.464	0.190	1.46 x 10^{-3}
4.0	4.06 x 10^{-2}	0.427	0.178	1.18 x 10^{-3}
4.2	4.03 x 10^{-2}	0.410	0.163	1.03 x 10^{-3}
4.4	3.91 x 10^{-2}	0.373	0.136	7.99 x 10^{-4}
4.6	3.62 x 10^{-2}	0.365	0.141	6.94 x 10^{-4}
4.8	3.43 x 10^{-2}	0.349	0.198	5.73 x 10^{-4}
5,0	3.42 x 10^{-2}	0.327	0.113	4.66 x 10^{-4}
5,5	3.00 x 10^{-2}	0.302	0.111	2.93 x 10^{-4}
6,0	2.77 x 10^{-2}	0.276	0.101	1.83 x 10^{-4}
6,5	2.82 x 10^{-2}	0.249	0.067	1.17 x 10^{-4}
7,0	2.68 x 10^{-2}	0.228	0.055	7.60 x 10^{-5}
7,5	2.60 x 10^{-2}	0.215	0.061	5.25 x 10^{-5}
8,0	2.62 x 10^{-2}	0.199	0.0474	3.62 x 10^{-5}
9,0	2.62 x 10^{-2}	0.174	0.0374	1.92 x 10^{-5}

$$\chi(\omega) = \chi_S + \frac{(\chi_T - \chi_S)}{1 + (i\omega\tau)^{1-\alpha}} \quad \text{Eq. S1}$$

$$\chi'(\omega) = \chi_S + (\chi_T - \chi_S)\frac{1 + (\omega\tau)^{1-\alpha}\sin\left(\pi\frac{\alpha}{2}\right)}{1 + 2(\omega\tau)^{1-\alpha}\sin\left(\pi\frac{\alpha}{2}\right) + (\omega\tau)^{2-2\alpha}} \quad \text{Eq. S2}$$

$$\chi''(\omega) = (\chi_T - \chi_S)\frac{(\omega\tau)^{1-\alpha}\cos\left(\pi\frac{\alpha}{2}\right)}{1 + 2(\omega\tau)^{1-\alpha}\sin\left(\pi\frac{\alpha}{2}\right) + (\omega\tau)^{2-2\alpha}}$$

Eq. S3



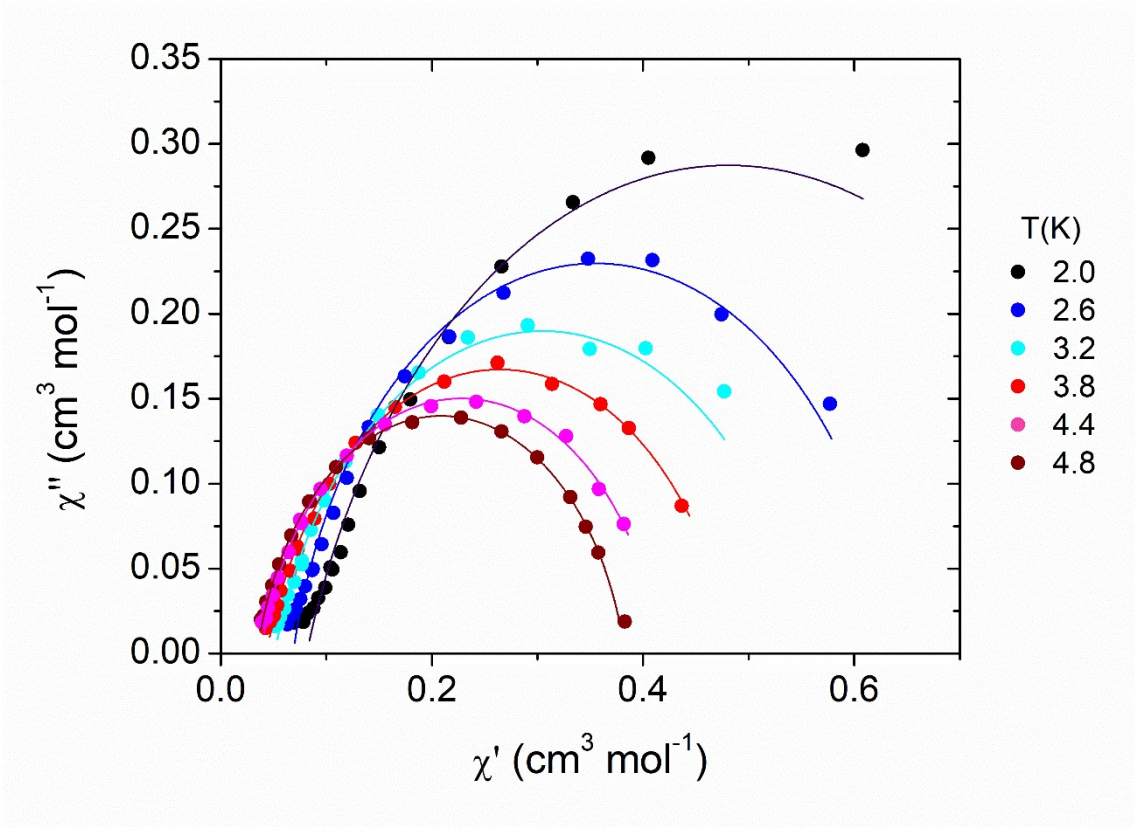


Fig. S19: Cole-Cole plot for **2b** at different temperatures using an applied DC field of 0.22 T. The lines represent the calculated curves using Eq. S2 and S3 using the parameters gathered in Table S8.

Table S9: Comparison between coordination environment of optimized structure of **2** and the experimental structure of **2a.**

	2a	**2**
	Bond Length (Å)	
Co - O1	2.136	2.111
Co - O2	2.035	2.026
Co - O3	2.106	2.236
	Bond Angle (°)	
O1 - Co - O2	80.6	80.8
O2 - Co - O1^{a}	99.4	99.2
O1^{a} - Co - O2^{a}	80.6	80.8
O2^{a} - Co - O1	99.4	99.2
O1 - Co - O1^{a}	180.0	180.0
O2 - Co - O2^{a}	180.0	180.0
O3 - Co – O3^{a}	180.0	180.0
O1 - Co - O3^{a}	86.1	84.6
O2 - Co - O3^{a}	88.2	98.4
O1^{a} - Co - O3^{a}	93.9	95.4
O2^{a} - Co - O3^{a}	91.8	81.6
O1 - Co - O3	93.9	95.4
O2 - Co - O3	91.8	81.6

O1[a] - Co - O3	86.1	84.6
O2[a] - Co - O3	88.2	98.4

[a] symmetry operation to generate equivalent atoms: -x+1/2,-y+3/2,-z+1

Table S10: xyz coordinates of optimized structure of **2**.

Co	1.900607000	2.049852000	11.572004000
O	1.992361000	2.015475000	9.463066000
N	1.741068000	3.537533000	7.736146000
C	3.032400000	1.651937000	4.206802000
O	1.021084000	3.832761000	11.181053000
C	2.511845000	2.947271000	4.182214000
H	2.434632000	3.489184000	3.244013000
O	-0.233949000	1.396944000	11.698880000
C	2.088404000	3.553840000	5.360165000
H	1.682646000	4.562724000	5.343328000
O	0.765439000	5.310751000	9.468391000
C	2.183110000	2.864588000	6.578441000
C	2.704417000	1.563193000	6.611547000
H	2.777273000	1.035625000	7.553902000
C	3.124609000	0.971247000	5.421411000
H	3.529793000	-0.036370000	5.449601000
C	1.668871000	3.140136000	9.014907000
C	1.099754000	4.230073000	9.957598000
H	1.401356000	4.499479000	7.644607000
H	-0.576414000	2.306415000	11.600745000
H	-0.492495000	0.930848000	10.886408000
O	4.035163000	2.702758000	11.445121000
H	4.377624000	1.793287000	11.543270000
H	4.293711000	3.168868000	12.257583000
O	1.808849000	2.084237000	13.680941000
O	2.780140000	0.266951000	11.962970000

N	2.060115000	0.562182000	15.407867000
C	0.768818000	2.447816000	18.937203000
C	1.289335000	1.152467000	18.961794000
H	1.366527000	0.610553000	19.899996000
C	1.712764000	0.545884000	17.783845000
H	2.118493000	-0.463011000	17.800685000
O	3.035813000	-1.211023000	13.675642000
C	1.618084000	1.235139000	16.565568000
C	1.096815000	2.536549000	16.532459000
H	1.023979000	3.064119000	15.590104000
C	0.676634000	3.128508000	17.722593000
H	0.271480000	4.136137000	17.694401000
C	2.132323000	0.959572000	14.129105000
C	2.701397000	-0.130386000	13.186413000
H	2.399800000	-0.399773000	15.499407000
H	3.363691000	1.178600000	3.287315000
H	0.437535000	2.921162000	19.856688000

Table S11: Calculated spin-free energy for the 7 first excited levels for **2a** and their contribution to the calculated ZFS parameters with NEVPT2.

State	2S+1	Energy / cm^{-1}	D contribution / cm^{-1}	E contribution / cm^{-1}
Q1	4	399.40	-120.44	-0.13
Q2	4	1153.10	20.22	-20.95
Q3	4	7902.90	-3.00	0.60
Q4	4	8032.50	-3.44	0.41
D1	2	9001.60	-3.72	-0.36
Q5	4	9824.70	4.99	-0.12
D2	2	12495.30	0.17	-0.71