Supplementary Information

Pentacoordinate Co(II) complex based on bulky tridentate and bidentate ligands with field-supported slow magnetic relaxation

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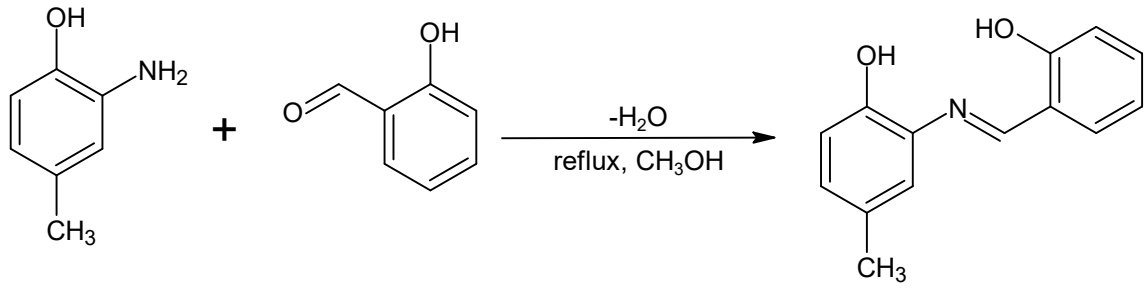

Scheme S1 Condensation reaction of synthesis of Schiff base H_2(*samphe*). The scheme was drawn by ChemDraw software [34].

Fig. S1 Single crystal of H_2(*samphe*)

Fig. S2 Single crystals of **1**

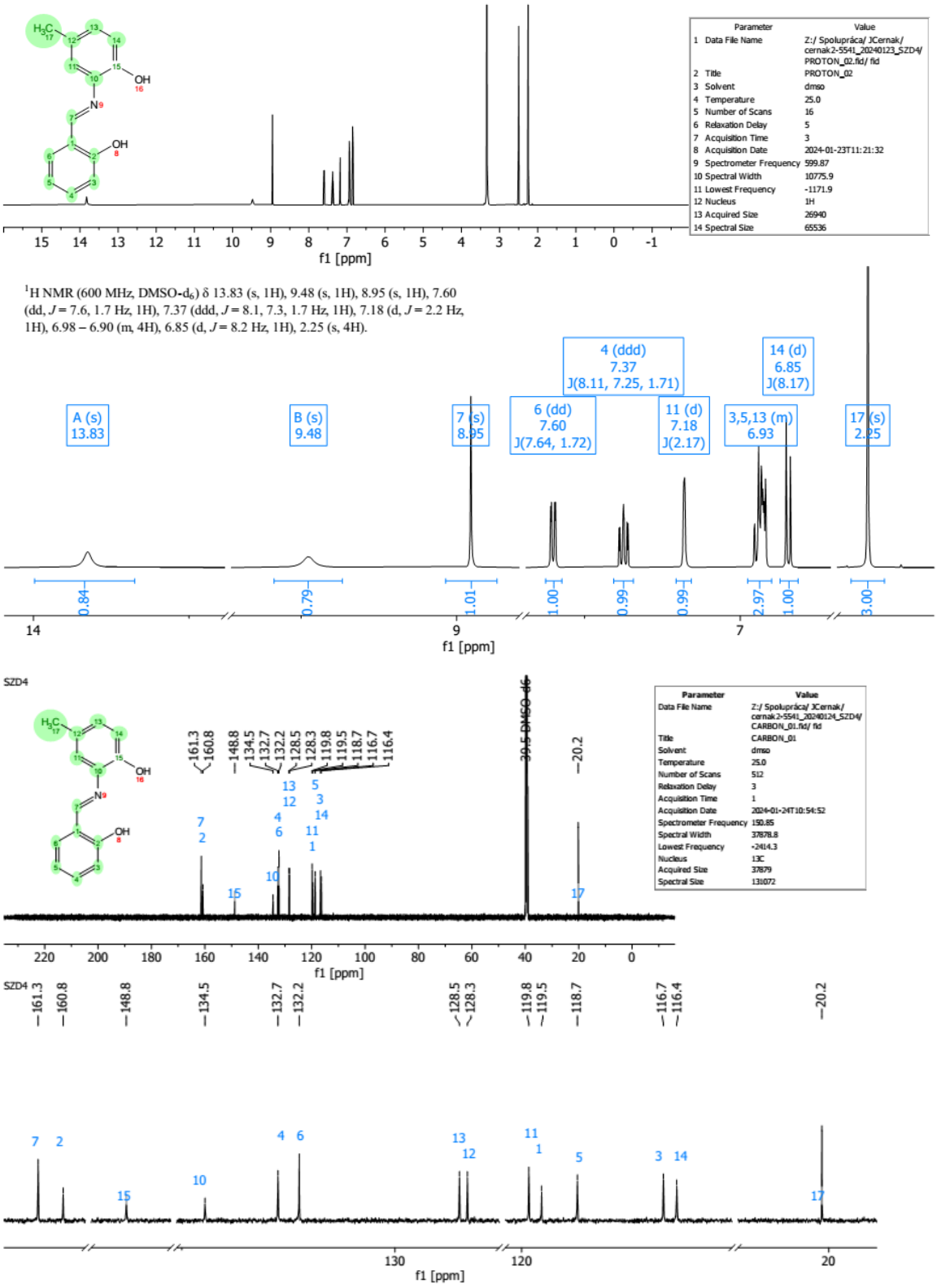

Fig. S3 ^{1}H NMR (upper) and ^{13}C NMR (below) spectra of H_2(*samphe*)

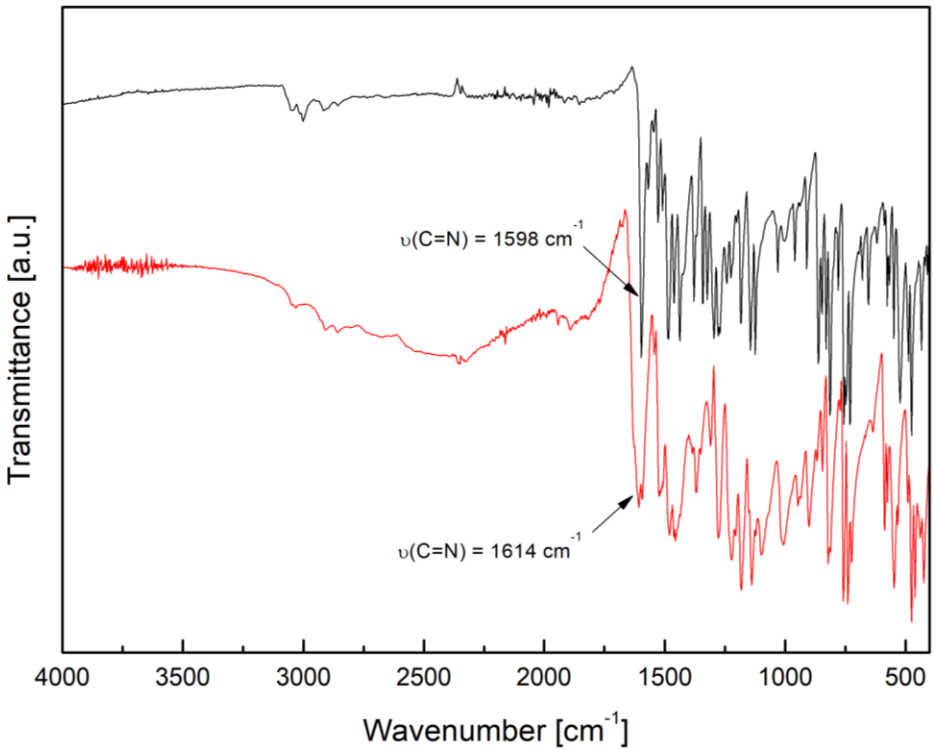

Fig S4 Infrared spectra of H_2(*samphe*) (red) and **1** (black).

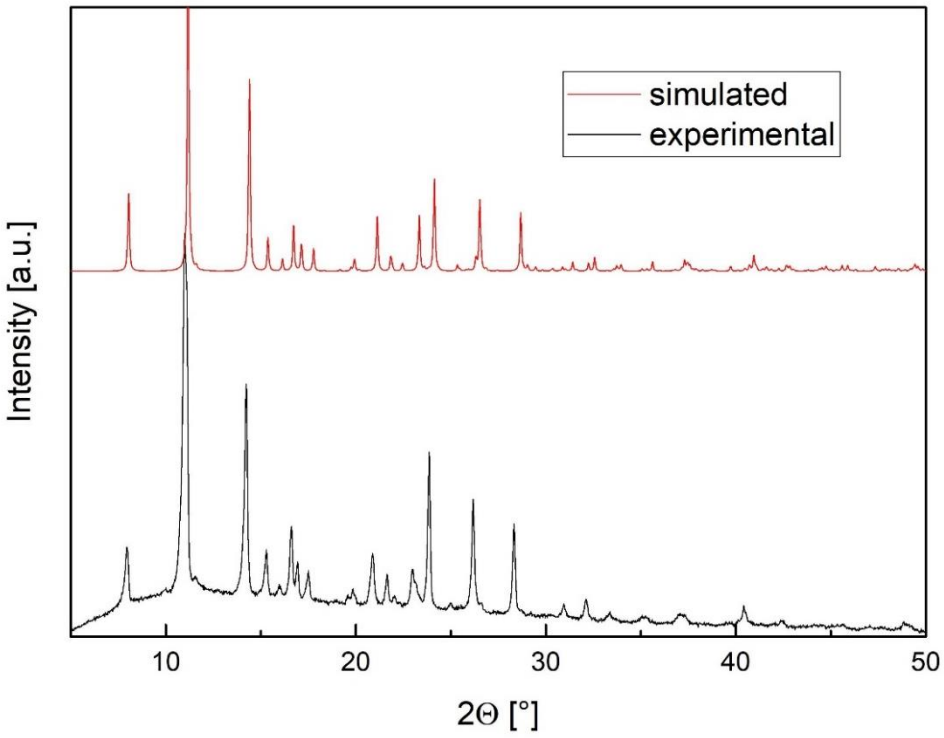

Fig S5 Experimental and simulated powder patterns of **1** plotted against each other.

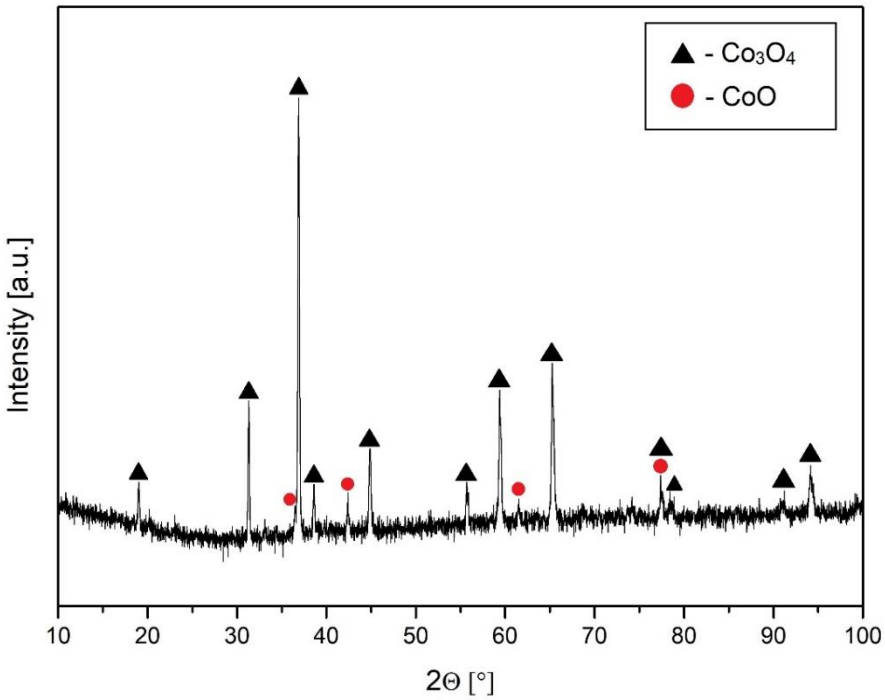

Fig. S6 Powder diffraction pattern of the solid residue after thermal decomposition of complex **1**.

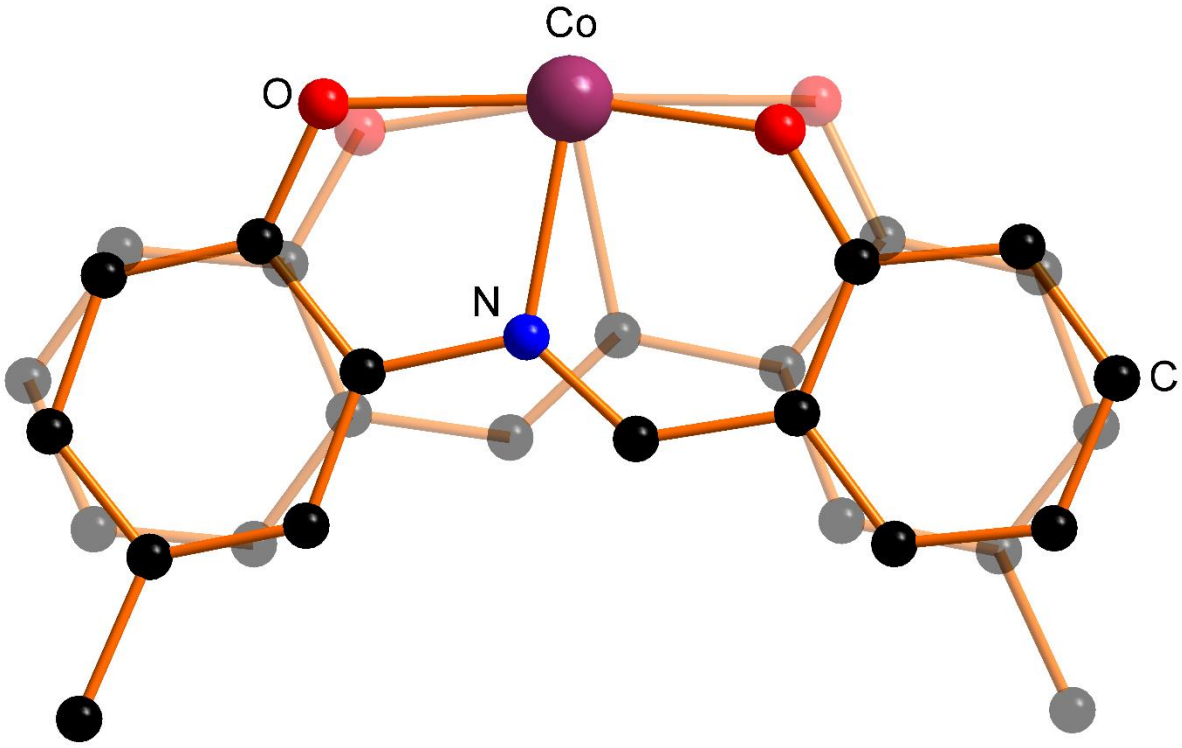

Fig. S7 Positional disorder of the Schiff base ligand (*samphe*)$^{2-}$ in **1**. The probability of the respective orientations is equal (50 %) due to internal symmetry 2.

Table S1 Geometric parameters of the π–π stacking interactions in complex **1.** From left to right, interaction between the centroids, distance between the centroids, dihedral angle α between the interacting planes and slippage are given. Values were calculated by PLATON software [31].

Cg(I)-*Cg*(J)	*Cg*···*Cg* [Å]	α [°]	β [°]	γ [°]	Slippage [Å]
*Cg*1-*Cg*2^{ii}	3.569(3)	2.7(3)	22.5	23.0	1.364

*Cg*1 is the center of gravity of the aromatic ring formed by N1 and C1-C5 atoms, *Cg*2 is the center of gravity of the aromatic ring formed by atoms C1, C2, C6, C1^{i}, C2^{i} a C6^{i}. Symmetry codes: i: 1-x, y, 3/2-z; ii: 1-y, 1-y, 1-z.

Table S2 Results of SHAPE analysis [63].

S H A P E v2.1 Continuous Shape Measures calculation (c) 2013 Electronic Structure Group, Universitat de Barcelona Contact: llunell@ub.edu

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a) Co(II) atom

PP-5	1	D5h	Pentagon
vOC-5	2	C4v	Vacant octahedron
TBPY-5	3	D3h	Trigonal bipyramid
SPY-5	4	C4v	Spherical square pyramid
JTBPY-5	5	D3h	Johnson trigonal bipyramid J12

Structure [ML5]	PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5
1	23.558	5.581	5.248	**4.986**	8.250

Table S3 Bonds and angles [Å, °] of **1**.

Co1-O1	1.88(2)	O1-C8	1.34(2)
Co1-O2	2.082(16)	C8-C9	1.390
Co1-N1	2.109(4)	C8-C13	1.390
Co1-N2	2.069(5)	C9-C10	1.390
N1-C1	1.356(5)	C9-C14	1.462(8)
N1-C5	1.326(6)	C10-C11	1.390
C1-C1^{i}	1.396(9)	C11-C12	1.390
C1-C2	1.420(5)	C12-C13	1.390
C2-C3	1.381(7)	C14-N2	1.286(8)
C2-C6	1.416(6)	N2-C16	1.399(6)
C3-C4	1.356(7)	O2-C15	1.351(19)
C4-C5	1.419(7)	C19-C20	1.390
C5-C7	1.498(7)	C15-C20	1.390
C6-C6^{i}	1.320(12)	C15-C16	1.390
C16-C17	1.390	C18-C21	1.554(8)
C17-C18	1.390	C18-C19	1.390
O1-Co1-O2	170.6(3)	O1-Co1-N1	95.6(7)
O1-Co1-N1^{i}	98.1(7)	O1-Co1-N2	91.5(6)
O2-Co1-N1	92.2(7)	O2-Co1-N1^{i}	88.6(6)
O2-Co1-N2	79.3(5)	N1-Co1-N1^{i}	78.0(2)
N1-Co1-N2	135.9(3)	N2-Co1-N1^{i}	143.7(2)
C5-N1-C1	118.1(4)	C5-N1-Co1	128.5(3)
C1-N1-Co1	113.3(3)	N1-C1-C1^{i}	117.6(3)
N1-C1-C2	123.1(4)	C1^{i}-C1-C2	119.3(3)
C3-C2-C6	123.6(5)	C3-C2-C1	117.0(4)
C6-C2-C1	119.5(5)	C4-C3-C2	120.3(5)
C3-C4-C5	119.8(5)	N1-C5-C4	121.6(5)
N1-C5-C7	116.6(4)	C4-C5-C7	121.7(5)

C6^{i}-C6-C2	121.2(3)	C8-O1-Co1	132.2(11)
O1-C8-C9	120.8(9)	O1-C8-C13	119.1(9)
C9-C8-C13	120.0	C10-C9-C8	120.0
C10-C9-C14	114.2(6)	C8-C9-C14	125.7(6)
C11-C10-C9	120.0	C10-C11-C12	120.0
C13-C12-C11	120.0	C12-C13-C8	120.0
N2-C14-C9	126.0(6)	C14-N2-Co1	123.3(4)
C16-N2-Co1	114.4(4)	C15-O2-Co1	111.6(9)
O2-C15-C16	121.1(8)	O2-C15-C20	118.8(8)
C16-C15-C20	120.0	C17-C16-C15	120.0
C17-C16-N2	126.6(5)	C15-C16-N2	113.4(5)
C18-C17-C16	120.0	C19-C18-C17	120.0
C19-C18-C21	120.4(5)	C17-C18-C21	119.3(5)
C20-C19-C18	120.0		

Symmetry code: i: 1-x, y, 3/2-z.

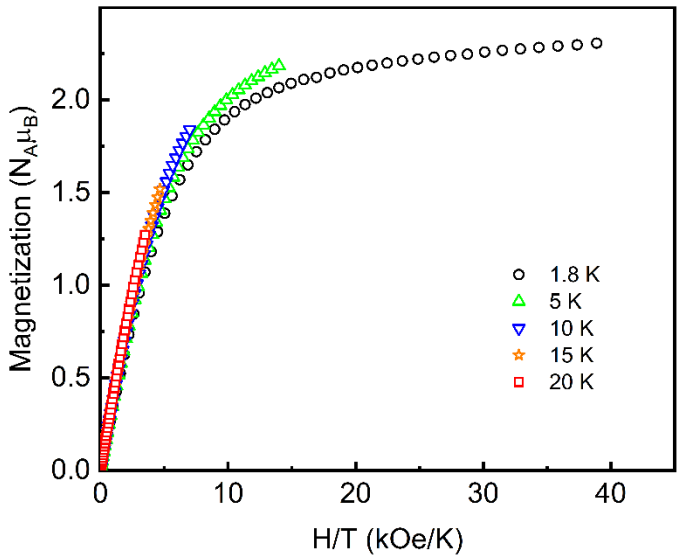

Fig. S8 The field dependence of magnetization (open symbols) in reduced coordinates.

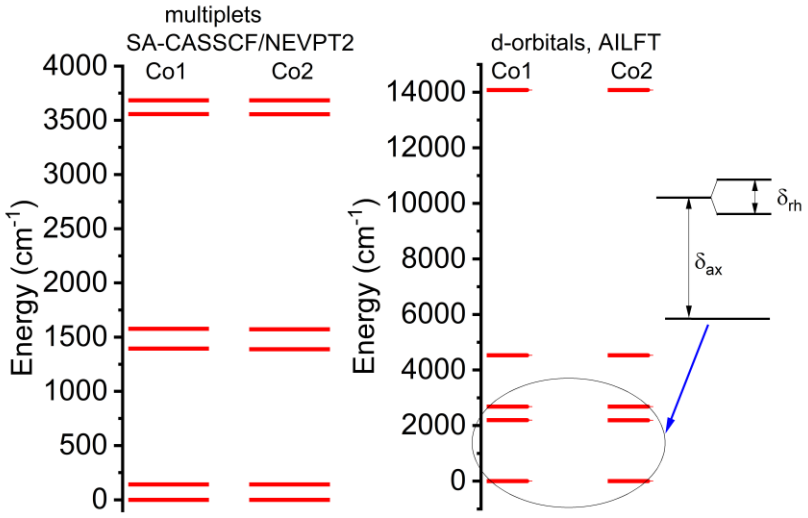

Fig. S9 The energies of 6 lowest multiplets as obtained from SA-CASSCF/NEVPT2 for **1**.

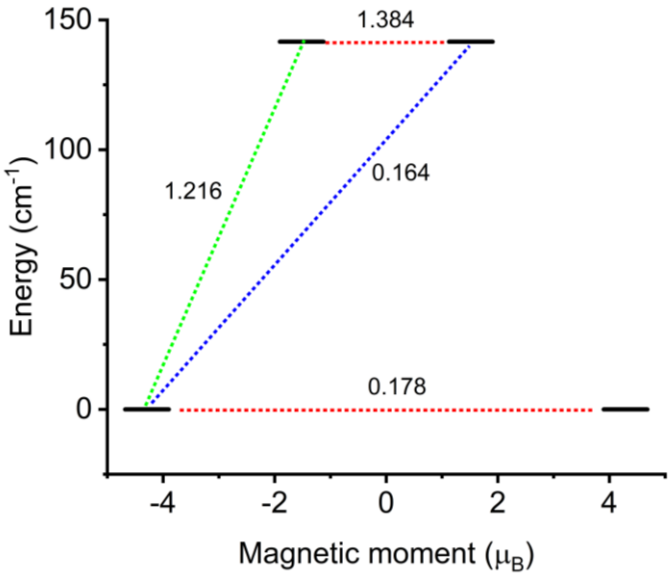

Fig S10 Transition probabilities between the energy levels of the two lowest Kramers doublets as obtained by *single_aniso* module in ORCA for **1**.

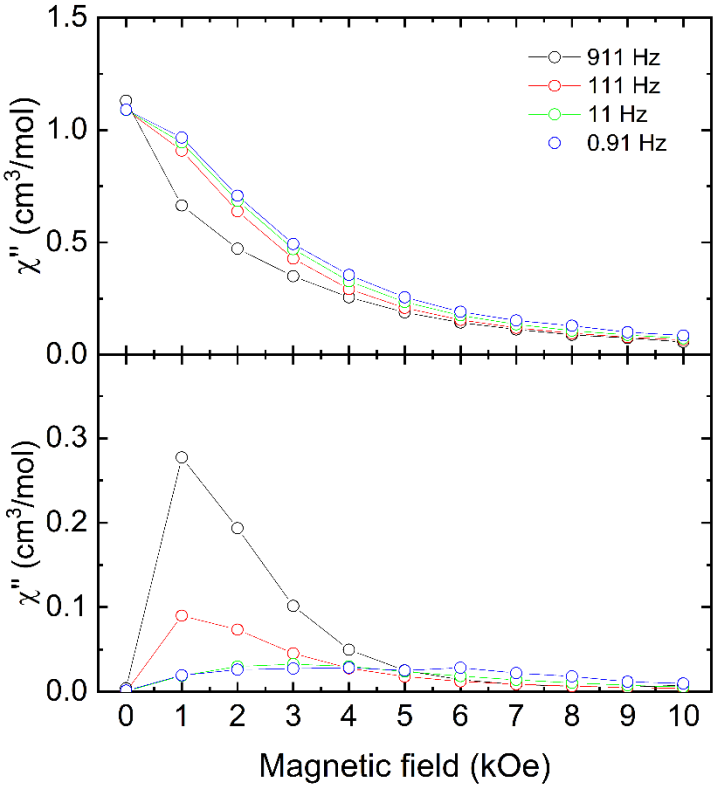

Fig. S11 Field dependence of AC susceptibility of **1** measured at 2 K with four different excitation frequencies in Quantum Design MPMS3.

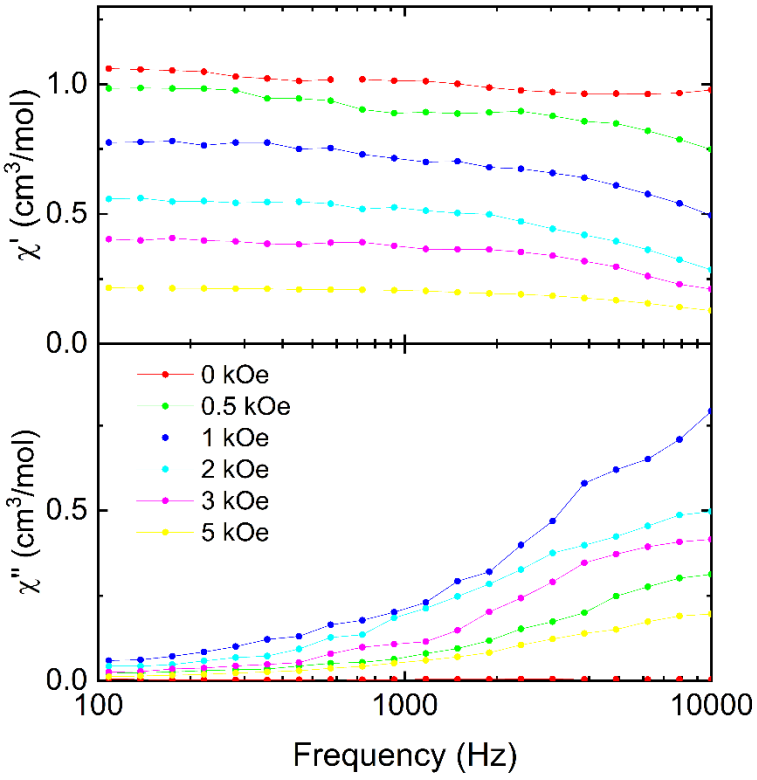

Fig. S12 Frequency dependence of AC susceptibility of **1** measured at 2 K at different applied static fields measured using the ACMS option of Quantum Design PPMS.

References

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