

Supplementary information for paper

Cobalt(II) paddle-wheel complex with 3,5-di(tert-butyl)-4-hydroxybenzoate bridges: DFT and *ab initio* calculations, magnetic dilution and magnetic properties

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1. IR spectra for 1-3

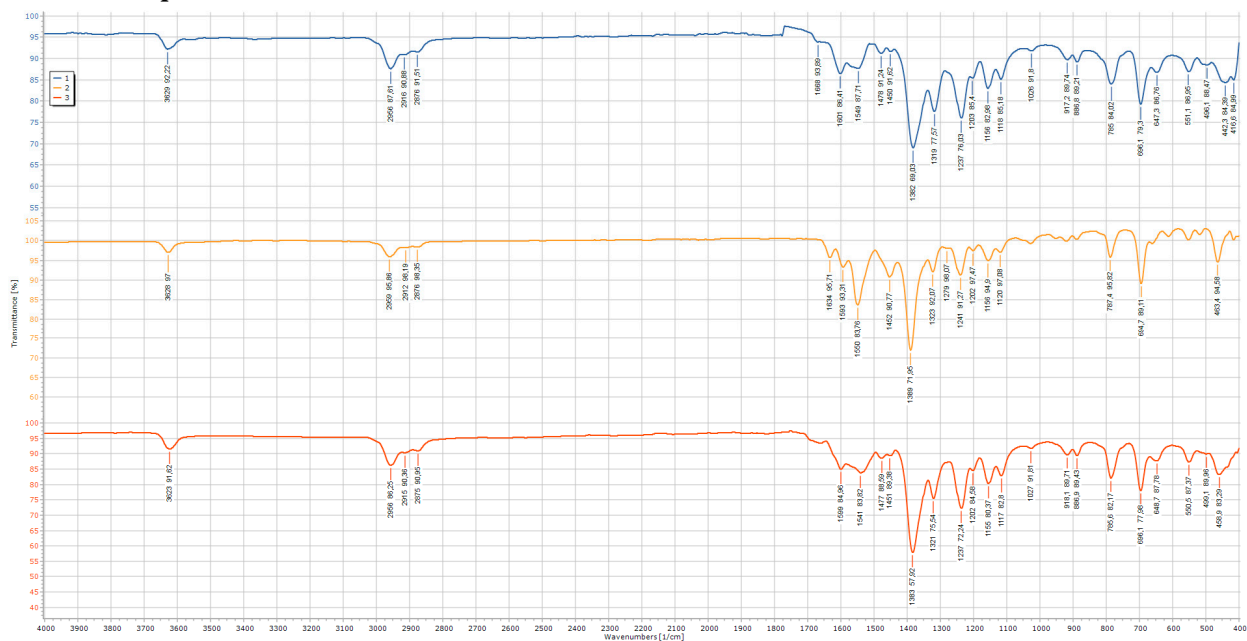


Fig. S1. IR spectra for 1-3

2. Raman spectra for 1-3

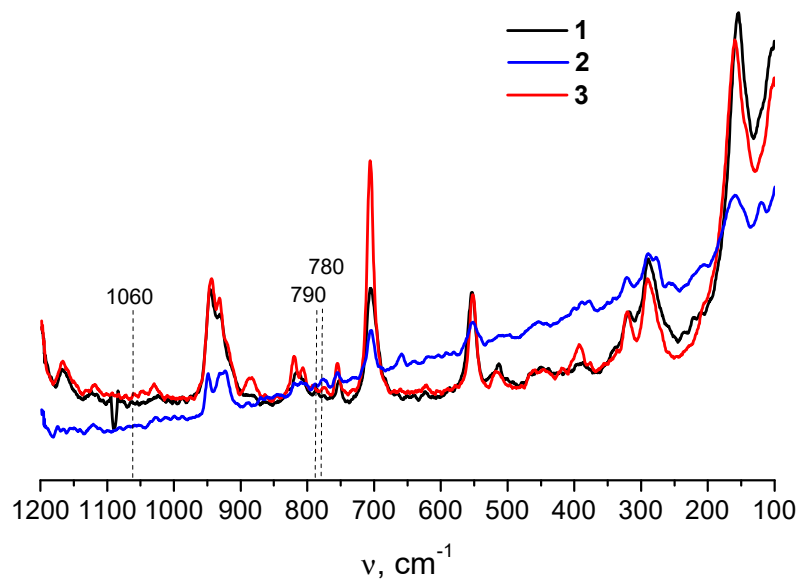


Fig. S2. Raman spectra for 1-3

3. PXRD for **1-3**

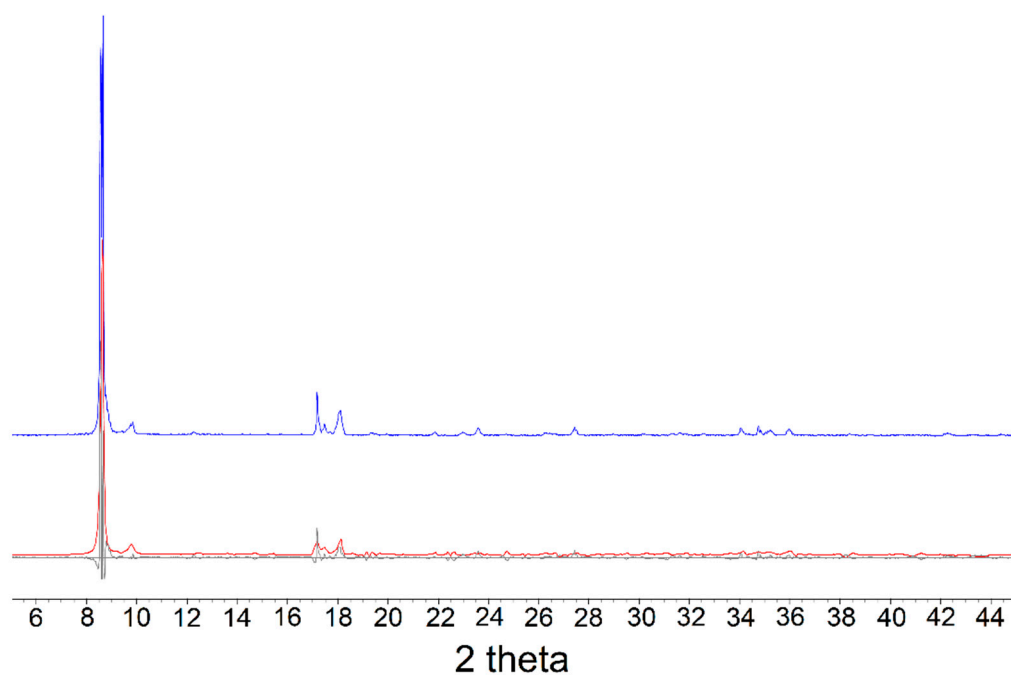


Fig. S3. Description of the diffractogram by the Rietveld method using the structure **1** (red curve - calculated, blue curve - experiment, gray curve - difference line; $\lambda = 1.54 \text{ \AA}$, at room temperature).

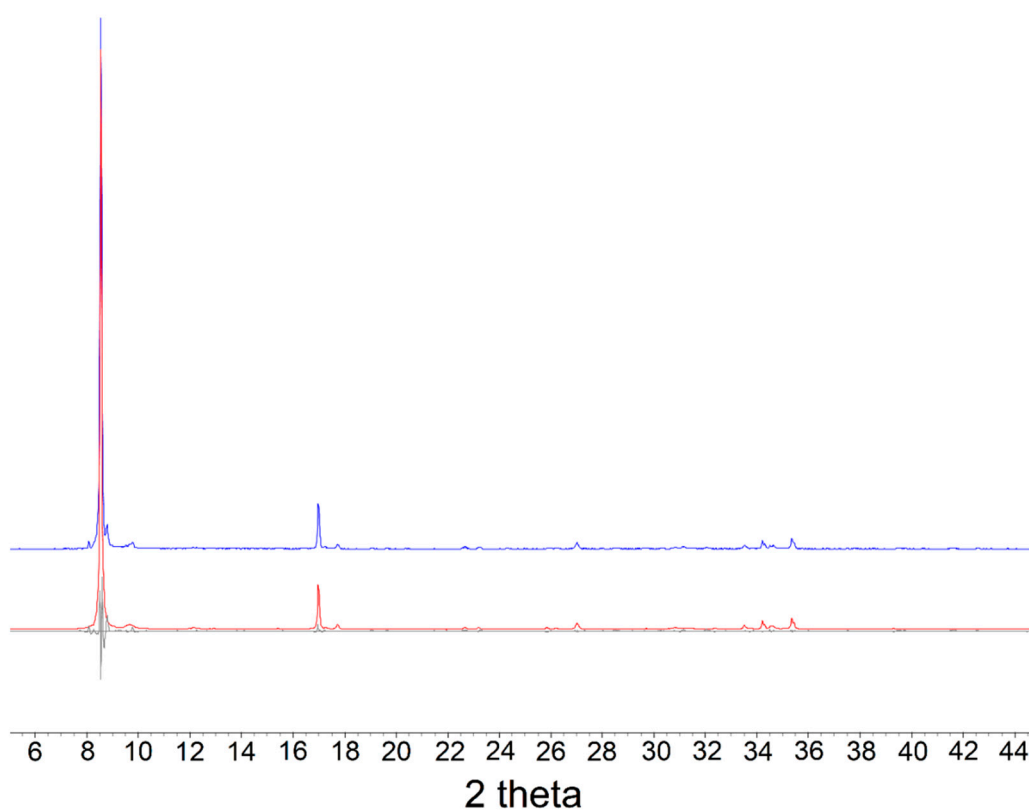


Fig. S4. Description of the diffractogram by the Rietveld method using the structure **2** (red curve - calculated, blue curve - experiment, gray curve - difference line; $\lambda = 1.54 \text{ \AA}$, at room temperature).

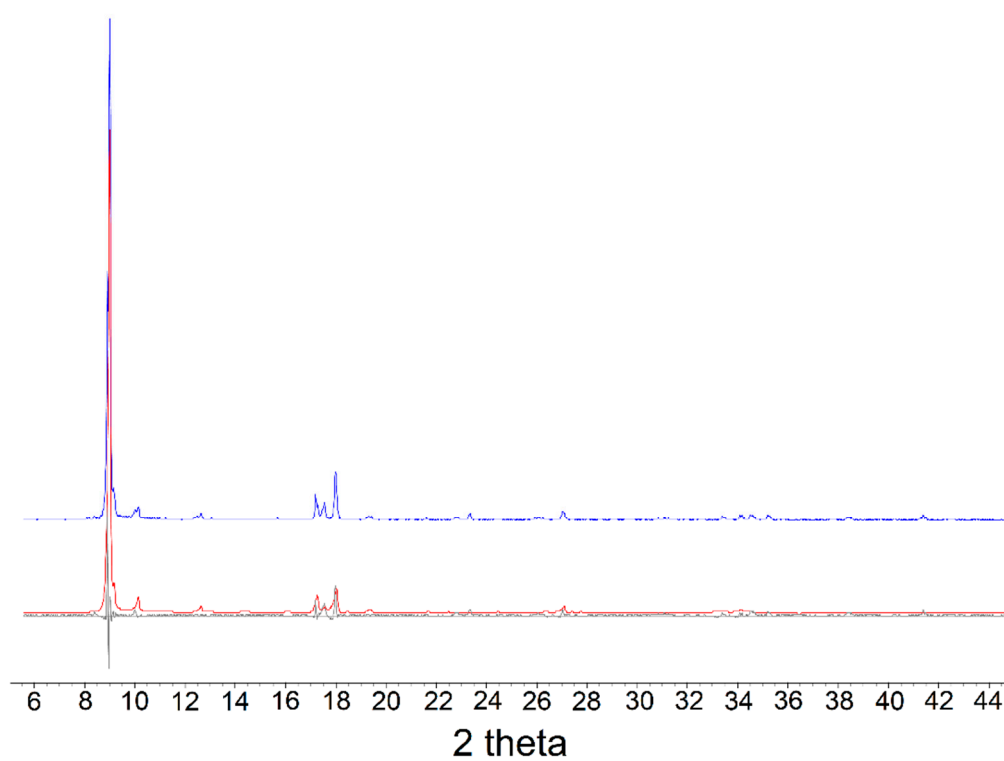


Fig. S5. Description of the diffractogram by the Rietveld method using the structure **3** (red curve - calculated, blue curve - experiment, gray curve - difference line; $\lambda = 1.54 \text{ \AA}$, at room temperature).

4. Table with parameters of D-H...O interactions in **1** and **2**

Table S1. Selected parameters for D-H...O interactions in **1** and **2**.

Interaction	D–H, Å	H...O, Å	D...O, Å	D–H–O, deg.
1				
O1S-H1S...O2S (1-x,-y,-z)	0.84	1.98	2.636(7)	134
O7-H7...O2S	0.95	1.87	2.618(5)	134
O7-H7...O1SA	0.95	2.59	3.210(10)	123
C3-H3A...O2	0.95	2.44	2.761(3)	100
C10-H10C...O3	0.98	2.45	3.103(7)	124
C11-H11B...O3	0.98	2.37	3.039(6)	125
C14-H14A...O3	0.98	2.35	2.970(5)	121
C15-H15A...O3	0.98	2.33	2.940(6)	119
C24-H24A...O6	0.98	2.41	3.059(4)	123
C26-H26A...O6	0.98	2.46	3.120(5)	124
C29-H29A...O6	0.98	2.35	2.976(5)	121
C30-H30B...O6	0.98	2.27	2.909(5)	122
C32-H32B...O5 (-x,-y,-z)	0.98	2.57	3.261(6)	127
2				
O1S-H1S...O2S (x,y,1+z)	0.82	1.89	2.707(5)	173
O7-H7...O2S	0.93	1.88	2.652(4)	139
O7-H7...O2SA	0.93	1.86	2.537(10)	127
C7-H7A...O2	0.93	2.46	2.776(2)	100
C10-H10A...O3	0.96	2.34	2.974(3)	123
C11-H11A...O3	0.96	2.29	2.934(3)	124
C14-H14A...O3	0.96	2.49	3.122(3)	123
C15-H15A...O3	0.96	2.41	3.058(3)	125
C18-H18...O5	0.93	2.47	2.781(2)	100
C22-H22...O4	0.93	2.48	2.793(2)	100
C24-H24A...O6	0.96	2.42	3.069(2)	124
C26-H26A...O6	0.96	2.5	3.132(2)	123
C29-H29B...O6	0.96	2.37	2.981(2)	121
C30-H30C...O6	0.96	2.28	2.917(3)	123
C32-H32C...O5 (-x,-y,-z)	0.96	2.58	3.266(3)	129

5. Table with parameters of C–H... π interactions in **1** and **2**

Table S2. C–H... π interactions in **1** and **2** (Cg is centroid of aromatic 6-membered ring).

C–H...Cg (symmetry)	H...Cg, Å	C–H–Cg, deg.	γ , deg.	C..Cg, Å
1				
C26–H26C...Cg(C17->C22) (-x,-1-y,-z)	2.87	156	16.79	3.785(4)
2				
C26–H26C...Cg(C17->C22) (-x,-1-y,-z)	2.96	156	20.20	3.854(2)

6. DFT calculations for **1** and CASSCF/NEVPT2/SINGLE_ANISO calculations for **3**

All quantum chemical calculations were performed with ORCA program package (version 5.0.1) [1] using the geometry of the experimentally determined X-ray structures. Broken-symmetry DFT calculations were performed using Becke's three parameters hybrid density functional [2] with the gradient-corrected correlation functional due to Lee, Yang, and Parr (B3LYP) [3] and convergence criteria. Subsequently, single point calculations were performed with various functionals to obtain final energies of the high-spin (HS) and the broken-symmetry (BS) states to calculate magnetic exchange coupling constant (J). The "flip spin" pattern was used to generate the initial state for the BS calculation. The energy difference between the high-spin and broken-symmetry solutions along with their spin expectation values were used in the Yamaguchi formalism [4] in the following equation.

$$J = -\frac{E_{HS} - E_{BS}}{S_{HS}^2 - S_{BS}^2}$$

Table S3. BS-DFT calculated energies of high-spin and broken-symmetry components, spin density and coupling constants for complex **1**

	Energy, Eh	ρ^{Co1}	ρ^{Co2}	$\langle S^2 \rangle$	J, cm^{-1}
HS	−6313.664491	2.676101	2.676101	12.0132	−62.73
BS	−6313.667078	−2.676096	2.676096	2.9655	

Ab initio calculations of ZFS parameters and g-tensor were performed based on state-averaged complete active space self-consistent field (SA-CASSCF) wave function [5] complemented by N-electron valence second-order perturbation theory (NEVPT2) [6]. To simplify and speed up the calculation procedure, *tert*-butyl substitutes were replaced by hydrogen atoms optimized with the B3LYP functional. The active space of the CASSCF calculations was made up of seven electrons in five d-orbitals of Co^{2+} ions. The state-averaged approach was used, in which all 10 quartet ($S = 3/2$) and 40 doublets ($S = 1/2$) states were averaged with equal weights. Here is the relativistic approximation Douglas–Kroll–Hess (DKH) [7] used in conjunction with appropriate polarized triple- ζ -quality basis set DKH-def2-TZVP was used for all atoms [8]. An auxiliary def2/JK Coulomb fitting basis set was used during the calculation [9]. ZFS parameters based on dominant spin-orbit coupling contributions from excited states were calculated through quasi-degenerate perturbation theory (QDPT) [10], with

the approximation to the Breit-Pauli form of the spin-orbit coupling operator (SOMF) [9] and an effective Hamiltonian approach [11]. The splitting of the d-orbitals was analyzed within the *ab initio* Ligand Field Theory (AILFT) [12]. The AILFT d-orbitals are described as their linear combinations, splitting is presented based on the largest coefficients for each orbital. The parameters of symmetry distortion of polyhedra from ideal point groups were calculated using the program ChemCraft (Version 1.8, build 648, <https://www.chemcraftprog.com>).

Input for calculations

```
!DKH DKH-def2-TZVP Def2/JK TightSCF SOMF(1X) PAL8
%maxcore 20000
%casscf
trafostep ri
nel 7
norb 5
ActOrbs dOrbs
mult 4, 2
nroots 10, 40
switchstep kdiis
orbstep superCI
maxiter 100
PTMethod SC_NEVPT2
rel
    DoSOC true
    GTensor true
    DTensor true
end
end
ANISO
    doaniso true
    MLTP 2,2,2,2
    TINT 0, 300, 301
    HINT 0, 7.0, 71
    TMAG 1.0, 1.2, 1.8, 2.5, 3.6
```

```

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CRY_charge 2
UBAR true
PLOT true
end

end
* xyz -2 4
541m.xyz
*

```

```

!B3LYP def2-TZVP D3BJ TightSCF PAL16
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%scf BrokenSym 3, 3
FlipSpin 1
FinalMs 0
end
* xyz 0 7
541d.xyz
*

```

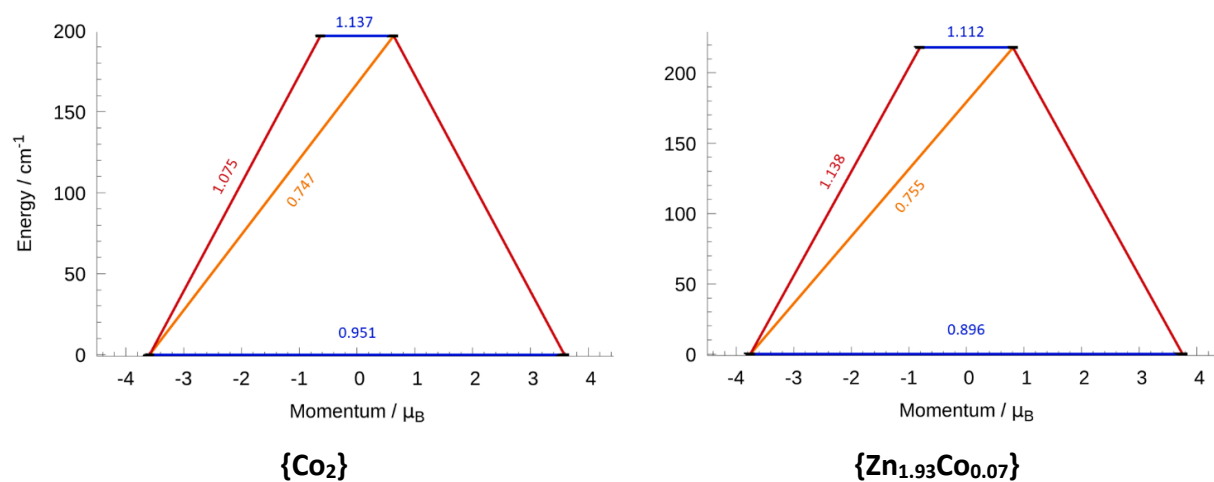


Fig. S6. CASSCF/NEVPT2/SINGLE_ANISO calculated splitting of two lowest Kramers doublets

(KDs) of the $^4A_2$ ground state for **1** (left) and ^4E_g for **3** (right), combined with their magnetic moments in the easy axis direction. Black lines imply KDs as a function of their magnetic moment; the red lines indicate the direct/Raman relaxation process; the blue lines correspond to the ground state QTM and thermally assisted-QTM via the first excited KD; the yellow line indicate the possible Orbach/Raman relaxation process [¹³; ¹⁴]. The average matrix elements of the transition magnetic moment between the ground states are quite high ($0.95 \mu_B$ for **1** and $0.90 \mu_B$ for **3**), which suggests a significant QTM suppressing relaxation in zero field [¹⁵].

7. Magnetic data for **3**

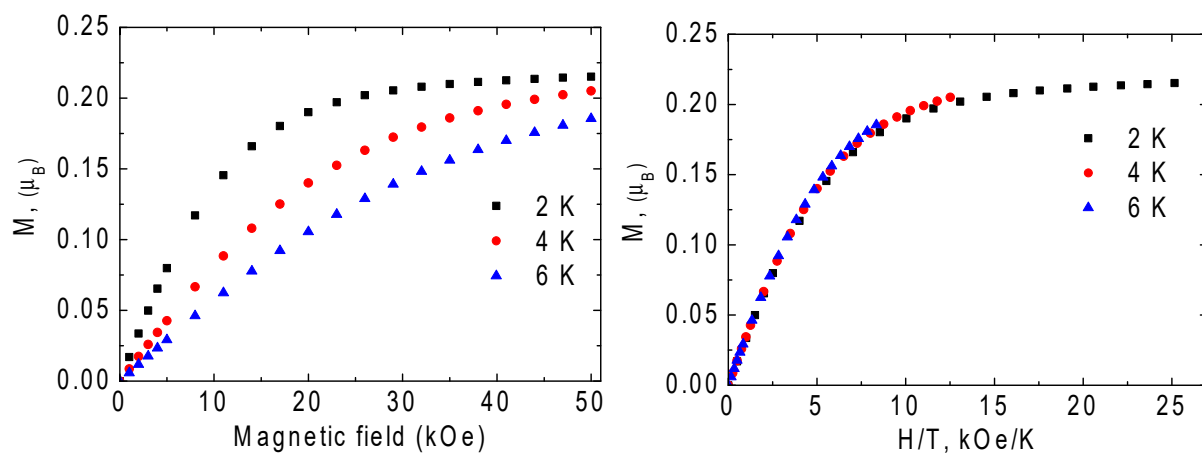


Fig. S7. The dependence of normalized magnetic moment M [μ_B] of the sample **3** from magnetic field strength (left) and H/T (right) at different temperatures.

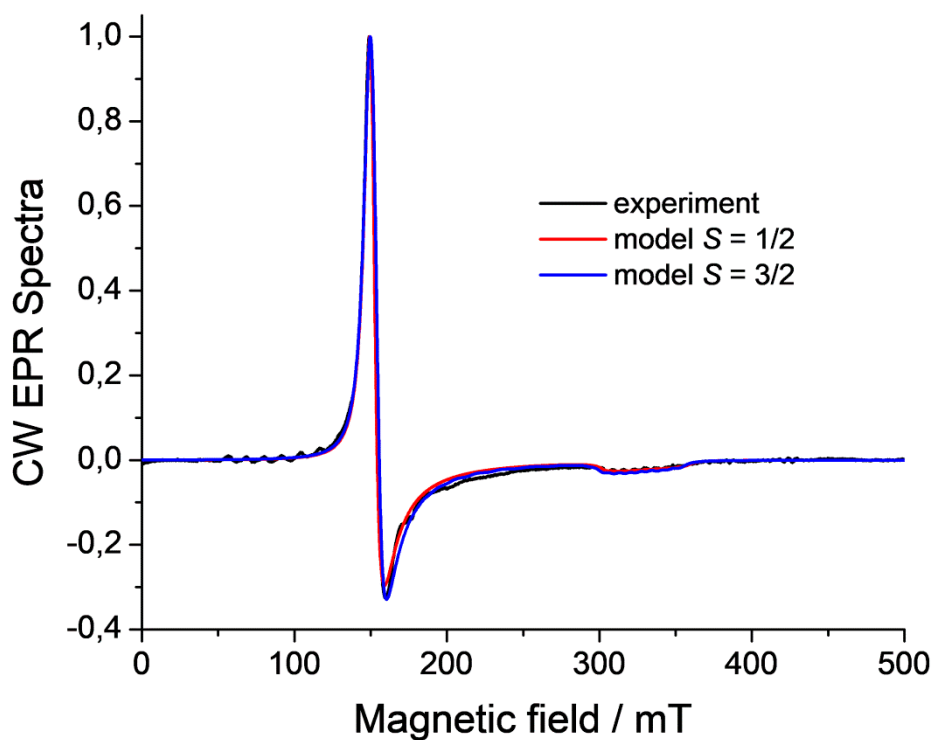


Fig. S8. X-band EPR spectrum of the complex **3** (polycrystalline sample, 10 K) and result of its simulation

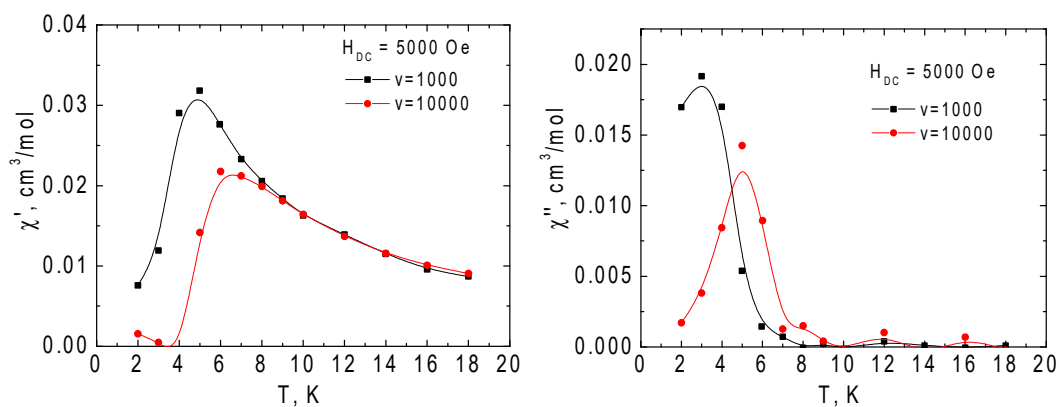


Fig. S9. Temperature dependences of the real (χ') and imaginary (χ'') part of dynamic magnetic susceptibility of the sample **3** at $H_{DC} = 5000$ Oe. The lines are visual guides.

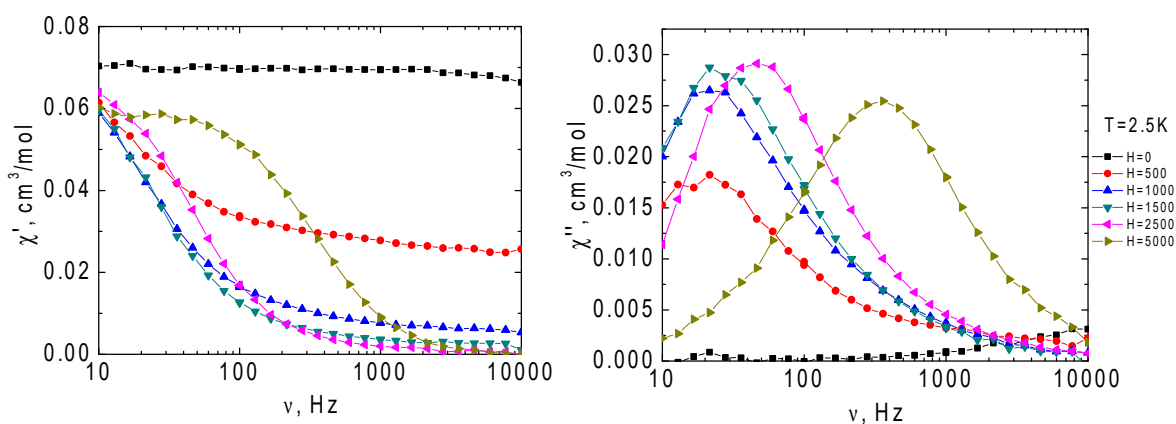


Fig. S10. The in-phase (χ') and out-of-phase (χ'') signal frequency dependences of the sample **3** at the variation of magnetic field strength ($T = 2.5$ K).

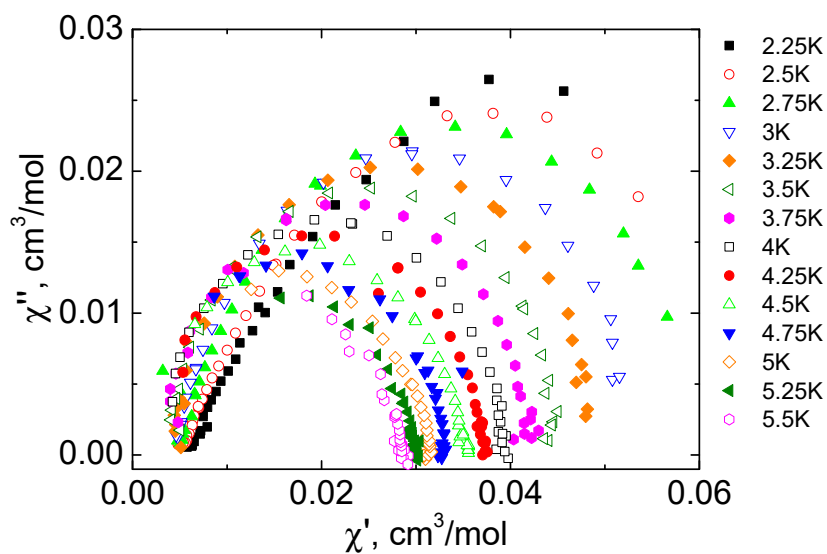


Fig. S11. Cole-Cole plots of the sample **3** under 1000 Oe dc-field at different temperatures.

8. References

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