

Electronic supplementary information (ESI)

Synthesis of **1**

Cobalt(II) acetate (1 mmol $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$, 0.2491 g) was dissolved in 20 cm^3 water and 2,6-dimethanolpyridine (2 mmol, 0.2783 g) washed down with 10 cm^3 of water and resulting mixture was few minutes stirred, then 3,5-dinitrobenzoic acid (2 mmol, 0.4242 g) was washed down with 10 cm^3 of water and resulting mixture was stirred for 2 hours and after filtration was left for crystal crystallization under ambient temperature. Light pink-red crystals were collected after four days, yield 0.199 g and were suitable for X-Ray data collection. Elemental analysis for $[\text{Co}(\text{pydm})_2](\text{dnbz})_2$; found: N 10.96, C 44.19, H 3.00, calc.: N 11.07, C 44.28, H 3.18 %.

Synthesis of **1a-1c**

According to the preparation steps of **1**, zinc dopants were prepared using cobalt(II) acetate and zinc(II) acetate in molar ratios Co:Zn as 0.5 mmol/0.5 mmol **1a**; 0.3 mmol/0.7 mmol **1b**; 0.7 mmol/0.3 mmol **1c**. Light pink-red crystals in all cases were obtained by a slow evaporation at the ambient temperature in six days. Colour intensity has been reduced in the order **1**, **1c**, **1a**, and **1b**. The exact content Co:Zn has been determined by single crystal X-ray structure analysis (see below). Yield: 0.090 g (**1a**), 0.080 g (**1b**), 0.110 g (**1c**).

Synthesis of **2**

Zinc (II) acetate (1 mmol $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, 0.2195 g) was dissolved in 20 cm^3 water and 2,6-dimethanolpyridine (2 mmol, 0.2783 g) washed down with 10 cm^3 of water and resulting mixture was few minutes stirred, then 3,5-dinitrobenzoic acid (2 mmol, 0.4242 g) was washed down with 10 cm^3 of water and resulting mixture was stirred for 2 hours and after filtration was left for crystal crystallization under ambient temperature. Colourless crystals were obtained by a slow evaporation at the ambient temperature in six days. Yield: 0.050 g.

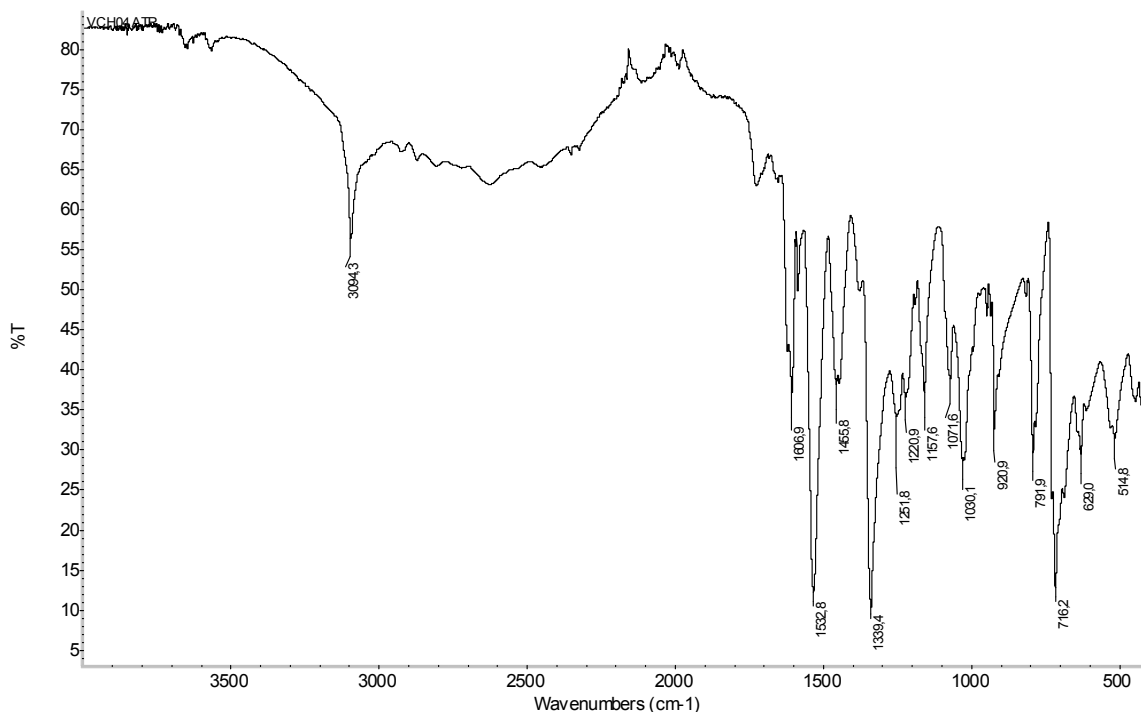


Figure S1. IR spectrum of **1**.

X-ray structure determination

Table S1. Crystal data and structure refinement for **1**, **1a**, **1b**, **1c** and **2**

	1	1c	1a	1b	2
Empirical formula	C ₂₈ H ₂₄ CoN ₆ O ₁₆	C ₂₈ H ₂₄ Co _{0.86} N ₆ O ₁₆ Zn _{0.14}	C ₂₈ H ₂₄ Co _{0.65} N ₆ O ₁₆ Zn _{0.35}	C ₂₈ H ₂₄ Co _{0.41} N ₆ O ₁₆ Zn _{0.59}	C ₂₈ H ₂₄ ZnN ₆ O ₁₆
Formula weight	759.46	760.36	761.71	763.26	765.90
Temperature/K	100	100	100	100	100
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1	P-1	P-1
a/Å	7.9759(4)	7.9916(3)	7.9844(2)	7.9833(2)	7.9839(2)
b/Å	13.8721(7)	13.8557(5)	13.8493(3)	13.8475(3)	13.8549(3)
c/Å	14.7030(7)	14.6907(5)	14.6890(4)	14.7060(4)	14.6856(3)
α/°	96.108(4)	96.040(3)	96.049(2)	96.090(2)	96.032(2)
β/°	105.136(4)	104.948(3)	104.960(2)	104.877(2)	104.763(2)
γ/°	100.589(4)	100.628(3)	100.467(2)	100.495(2)	100.517(2)
Volume/Å ³	1523.03(14)	1524.55(10)	1523.17(7)	1524.83(7)	1524.69(6)
Z	2	2	2	2	2
ρ _{calc} /g/cm ³	1.656	1.656	1.661	1.662	1.668
μ/mm ⁻¹	5.231	4.765	4.077	3.282	1.932
F(000)	778.0	779.0	780.0	782.0	784.0
Crystal size/mm ³	0.23 × 0.21 × 0.1	0.35 × 0.25 × 0.25	0.45 × 0.35 × 0.35	0.35 × 0.35 × 0.35	0.45 × 0.35 × 0.35
Radiation	CuKα (λ = 1.54186)	CuKα (λ = 1.54186)	CuKα (λ = 1.54186)	CuKα (λ = 1.54186)	CuKα (λ = 1.54186)
2θ range for data collection/°	6.312 to 143.334	6.576 to 142.624	6.31 to 143.268	6.3 to 142.512	6.304 to 142.48
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 16, -18 ≤ l ≤ 13	-5 ≤ h ≤ 9, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17	-9 ≤ h ≤ 7, -17 ≤ k ≤ 15, -18 ≤ l ≤ 16	-9 ≤ h ≤ 9, -17 ≤ k ≤ 16, -8 ≤ l ≤ 17	-9 ≤ h ≤ 8, -8 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	34832	31090	32880	33083	40949
Independent reflections	5753 [R _{int} = 0.0982, R _{sigma} = 0.0554]	5710 [R _{int} = 0.0649, R _{sigma} = 0.0452]	5759 [R _{int} = 0.0439, R _{sigma} = 0.0225]	5740 [R _{int} = 0.0217, R _{sigma} = 0.0145]	5699 [R _{int} = 0.0232, R _{sigma} = 0.0110]
Data/restraints/parameters	5753/0/460	5710/0/461	5759/0/462	5740/0/462	5699/0/461
Goodness-of-fit on F ²	0.948	1.066	1.085	1.018	1.105
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0367, wR ₂ = 0.0887	R ₁ = 0.0776, wR ₂ = 0.2370	R ₁ = 0.0402, wR ₂ = 0.1083	R ₁ = 0.0239, wR ₂ = 0.0580	R ₁ = 0.0308, wR ₂ = 0.0772
Final R indexes [all data]	R ₁ = 0.0410, wR ₂ = 0.0901	R ₁ = 0.0964, wR ₂ = 0.2552	R ₁ = 0.0423, wR ₂ = 0.1111	R ₁ = 0.0265, wR ₂ = 0.0591	R ₁ = 0.0314, wR ₂ = 0.0776
Largest diff. peak/hole / e Å ⁻³	0.54/-0.50	1.80/-0.74	0.46/-0.52	0.29/-0.29	0.41/-0.46
CCDC code	1533249	1562423	1562424	1562425	1562426

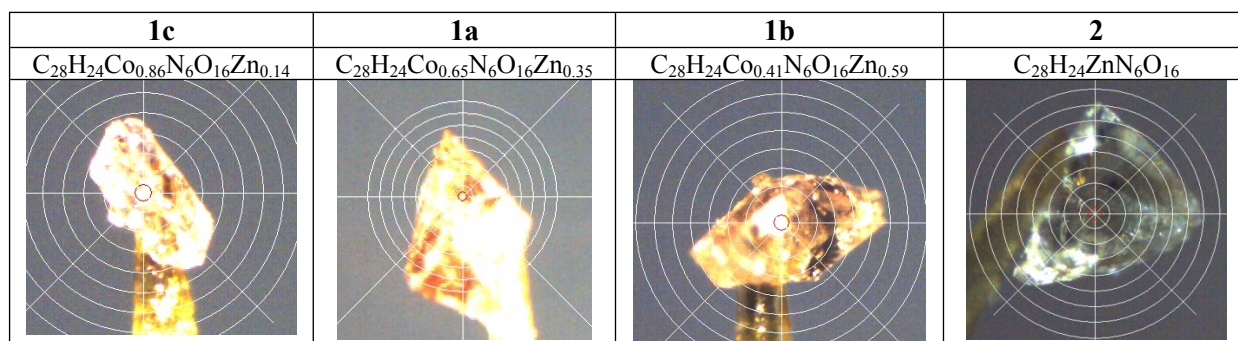


Figure S2. Single crystals mounted at the diffractometer.

Table S2. Bond lengths and bond angles in **1**.

Co1	O1	2.1455(13)					
Co1	O2	2.0777(13)					
Co1	O3	2.1855(14)					
Co1	O4	2.1580(13)					
Co1	N1	2.0364(16)					
Co1	N2	2.0403(16)					
O1	Co1	O3	95.71(5)	N1	Co1	O1	76.65(6)
O1	Co1	O4	89.46(5)	N1	Co1	O2	77.68(6)
O2	Co1	O1	151.88(5)	N1	Co1	O3	91.06(6)
O2	Co1	O3	96.06(5)	N1	Co1	O4	114.76(6)
O2	Co1	O4	90.96(5)	N1	Co1	N2	166.77(6)
O4	Co1	O3	154.16(5)	N2	Co1	O1	99.31(6)
				N2	Co1	O2	108.22(6)
				N2	Co1	O3	76.70(6)
				N2	Co1	O4	77.48(6)

Table S3 Hydrogen Bonds in **1**.

D–H	A	d(D–H)/Å	d(H–A)/Å	d(D–A)/Å	D–H–A/°
O1–H1	⋯O11	0.87	1.70	2.559(2)	167
O2–H2	⋯O6	0.87	1.66	2.533(2)	177
O3–H3	⋯O12	0.87	1.74	2.592(2)	165
O4–H4	⋯O5	0.87	1.75	2.586(2)	159

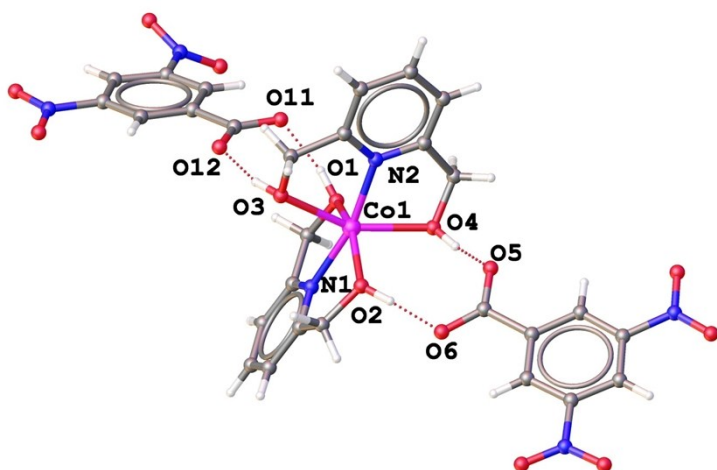


Figure S3. Labelling of atoms for the identification of metal-ligand and hydrogen bonds in **1**.

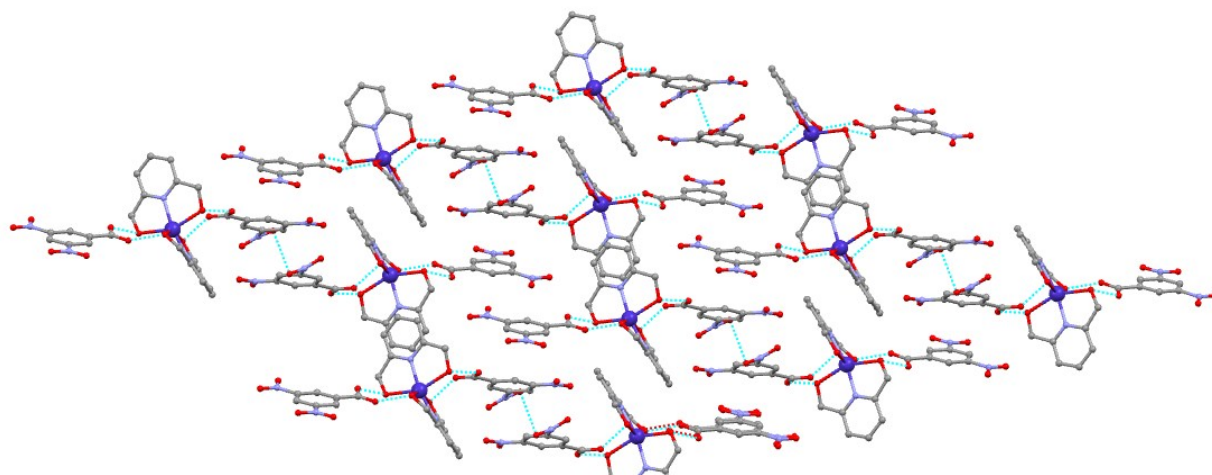


Figure S4. View of the crystal packing for **1**.

Electronic spectra

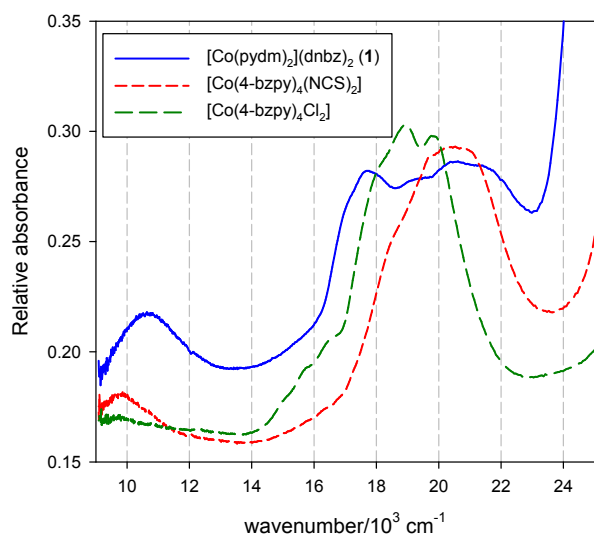


Figure S5. Solid-state UV-Vis absorption spectrum for **1** (solid) taken in the Nujol suspension (Specord 250 Plus spectrometer, Analytica Jena). Peak assignment in the octahedral approximation: ${}^4T_{2g} \leftarrow {}^4T_{1g}(\text{F})$ [10600], ${}^4A_{2g} \leftarrow {}^4T_{1g}(\text{F})$ [17700] and ${}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g}$ [20500 cm^{-1}]. Spectra of square bipyramidal complexes $[\text{Co}(4\text{-bzpy})_4(\text{NCS})_2]$ and $[\text{Co}(4\text{-bzpy})_4\text{Cl}_2]$ complexes (dashed, red and green, respectively) are drawn for comparison.

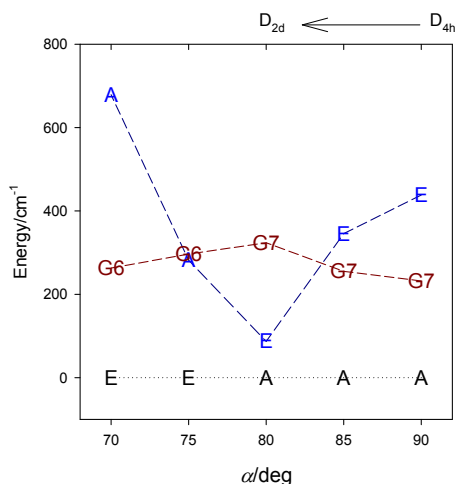


Figure S6. Calculated energies of the crystal field terms (A, E) and multiplets (G6, G7) on angular distortion of square pyramid D_{4h} to D_{2d} via angle α bisecting O-Co-O. Expt.: $2\alpha = \text{O2-Co1-O1} = 151.88$ and $\text{O4-Co1-O3} = 154.16$ deg.

FT-IR spectra

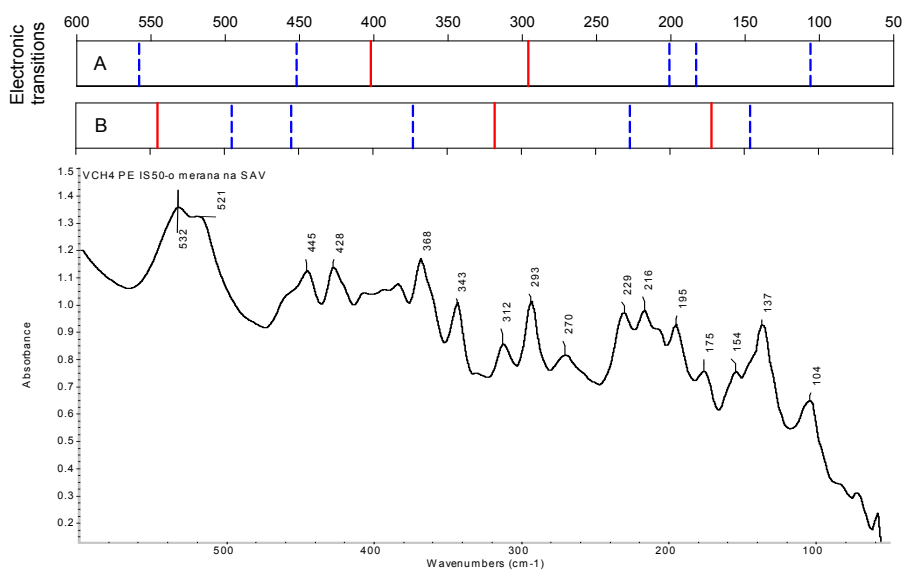


Figure S7. FT-IR spectra in the Far region. Band A – calculated electronic transitions by the crystal field model; band B – calculated by the Griffith-Figgis model of the magnetic data fitting; solid-red – from the ground multiplet, dashed-blue – among excited multiplets.

Table S4. Calculated electronic transitions in the Far-IR region

A) according to the crystal field model

	$1\Gamma_6$	$2\Gamma_6$	$1\Gamma_7$	$2\Gamma_7$	$3\Gamma_6$
$2\Gamma_6$	296	-			
$1\Gamma_7$	402	106	-		
$2\Gamma_7$	854	558	452	-	
$3\Gamma_6$	1037	741	635	183	-
$3\Gamma_7$	1055	759	653	201	18

B) by magnetic data fitting (Griffith-Figgis model)

	$1\Gamma_6$	$2\Gamma_6$	$1\Gamma_7$	$2\Gamma_7$	$3\Gamma_6$
$2\Gamma_6$	172	0			
$1\Gamma_7$	318	146	0		
$2\Gamma_7$	545	373	227	0	
$3\Gamma_6$	1000	828	682	455	0
$3\Gamma_7$	1040	868	722	495	40

C) by *ab initio* (ORCA) calculations

	$1\Gamma_6$	$2\Gamma_6$	$1\Gamma_7$	$2\Gamma_7$	$3\Gamma_6$
$2\Gamma_6$	194	-			
$1\Gamma_7$	876	682	-		
$2\Gamma_7$	1111	917	235	-	
$3\Gamma_6$	2487	2293	1611	1376	-
$3\Gamma_7$	2573	2379	1697	1462	86

AC susceptibility

Fitting of the AC susceptibility data is based upon 44 data points (22 in-phase and 22 out-of-phase) using the formula for the **two-set Debye model**

$$\chi(\omega) = \chi_S + \frac{\chi_{T1} - \chi_S}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{\chi_{T2} - \chi_{T1}}{1 + (i\omega\tau_2)^{1-\alpha_2}} \text{ or}$$

$$\chi(\omega) = \chi_S + (\chi_T - \chi_S) \left[\frac{x_1}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{1-x_1}{1 + (i\omega\tau_2)^{1-\alpha_2}} \right]$$

where x_1 is the weight of the first, low-frequency relaxation set (channel, branch). This equation decomposes into two explicit formulae for

a) the in-phase component

$$\chi'(\omega) = \chi_S + (\chi_{T1} - \chi_S) \frac{1 + (\omega\tau_1)^{1-\alpha_1} \sin(\pi\alpha_1/2)}{1 + 2(\omega\tau_1)^{1-\alpha_1} \sin(\pi\alpha_1/2) + (\omega\tau_1)^{2-2\alpha_1}} + (\chi_{T2} - \chi_{T1}) \frac{1 + (\omega\tau_2)^{1-\alpha_2} \sin(\pi\alpha_2/2)}{1 + 2(\omega\tau_2)^{1-\alpha_2} \sin(\pi\alpha_2/2) + (\omega\tau_2)^{2-2\alpha_2}}$$

b) the out-of-phase component

$$\chi''(\omega) = (\chi_{T1} - \chi_S) \frac{(\omega\tau_1)^{1-\alpha_1} \cos(\pi\alpha_1/2)}{1 + 2(\omega\tau_1)^{1-\alpha_1} \sin(\pi\alpha_1/2) + (\omega\tau_1)^{2-2\alpha_1}} + (\chi_{T2} - \chi_{T1}) \frac{(\omega\tau_2)^{1-\alpha_2} \cos(\pi\alpha_2/2)}{1 + 2(\omega\tau_2)^{1-\alpha_2} \sin(\pi\alpha_2/2) + (\omega\tau_2)^{2-2\alpha_2}} w$$

with the constraint for the isothermal susceptibilities $\chi_{T1} < \chi_{T2}$ in order to get positive contributions from each primitive component. Then $x_1 = (\chi_{T1} - \chi_S) / (\chi_{T2} - \chi_S) = (\chi_S - \chi_{T1}) / (\chi_S - \chi_{T2})$.

Seven free parameters (χ_S , χ_{T1} , χ_{T2} , α_1 , α_2 , τ_1 , and τ_2) can be fitted reliably by using 44 experimental data points. The functional to be minimized accounts to the relative errors of both susceptibility components

- $F = w \cdot E(\chi') + (1-w) \cdot E(\chi'')$ with the typical weight $w = 0.07$, or

- $F = E(\chi') \cdot E(\chi'')$ with $E(\chi) = (1/N) \left[\sum_i^N |(\chi_i^e - \chi_i^c) / \chi_i^c| \right]$

Table S5. Results of the fitting procedure for AC susceptibility components of **1**.

a) at $B_{DC} = 0.2$ with a two-set Debye model

T/K	$R(\chi')$ /%	$R(\chi'')$ /%	χ_S	χ_{LF}	α_{LF}	τ_{LF} / 10^{-3} s	χ_{HF}	α_{HF}	τ_{HF} / 10^{-3} s	χ_{LF}
1.9	0.47	1.7	0	4.8(7)	0.21(3)	29(2)	9.9(1)	0.47(1)	2.6(8)	0.48
2.1	0.52	1.9	0	4.5(8)	0.21(3)	22(1)	9.0(1)	0.46(1)	2.1(8)	0.50
2.3	0.48	2.3	0.06(6)	4.2(13)	0.22(5)	17(2)	8.4(1)	0.44(4)	1.7(11)	0.50
2.5	0.89	2.3	0.10(11)	4.0(23)	0.24(8)	13(3)	7.7(1)	0.42(7)	1.4(14)	0.51
2.7	0.81	2.8	0.19(10)	4.1(12)	0.25(4)	10(2)	7.1(1)	0.34(7)	0.90(46)	0.57
2.9	0.50	2.3	0.29(4)	3.6(4)	0.21(2)	9.8(8)	7.6(1)	0.27(3)	0.70(9)	0.45
3.1	0.58	2.3	0.23(5)	3.0(3)	0.16(1)	8.7(6)	6.2(1)	0.26(3)	0.54(5)	0.46
3.3	0.60	2.4	0.20(7)	2.5(2)	0.10(2)	7.2(4)	5.8(1)	0.25(3)	0.40(3)	0.41
3.5	0.59	2.6	0.11(9)	1.9(3)	0.03(3)	6.1(3)	5.5(1)	0.29(4)	0.33(3)	0.33
3.7	0.54	2.5	0.13(11)	2.0(3)	0.01(2)	4.6(2)	5.2(1)	0.26(3)	0.21(1)	0.37
4.1	0.67	1.8	0.20(2)	2.1(4)	0.01(2)	2.3(1)	4.7(1)	0.20(7)	0.096(9)	0.42
4.5	0.31	1.4	0.07(40)	1.9(5)	0.01(1)	1.3(1)	4.3(1)	0.18(8)	0.043(11)	0.43
4.9	0.26	1.4	0	1.75(6)	0.01(1)	0.75(1)	4.0(1)	0.19(4)	0.021(1)	0.44

b) at $B_{DC} = 0.4$ with a two-set or three-set Debye model

T/K	$R(\chi')$ /%	$R(\chi'')$ /%	χ_S	χ_{LF}	α_{LF}	τ_{LF} / 10^{-3} s	χ_{HF}	α_{HF}	τ_{HF} / 10^{-3} s	χ_{HF}	α_{HF}	τ_{HF} / 10^{-3} s
1.9	0.48	1.5	0.08(3)	4.1(1)	0.33(1)	131(4)				8.9(1)	0.28(1)	0.96(2)
2.3	0.62	2.0	0.18(3)	2.7(1)	0.32(2)	126(7)				7.7(1)	0.26(1)	1.00(2)
2.7	0.75	2.5	0.23(3)	1.8(1)	0.31(4)	121(11)				6.8(1)	0.23(1)	0.87(2)
3.1	0.44	2.2	0.23(2)	1.1(1)	0.21(4)	172(11)				6.0(1)	0.24(1)	0.69(1)
3.5	0.68	3.3	0.21(4)	0.60(7)	0.02(8)	250(30)				5.3(1)	0.27(1)	0.49(1)
3.5	0.49	1.9	0.03(18)	0.70(32)	0.26(9)	212(42)	2.3(21)	0.05(16)	1.11(25)	5.5(1)	0.27(12)	0.22(17)
3.9	0.48	2.0	0.48(11)	0.99(13)	0.40(8)	284(61)	2.7(4)	0.01(4)	1.12(10)	5.0(1)	0.09(7)	0.15(11)
4.3	0.62	2.1	0.50(41)	0.86(47)	0.50(18)	387(275)	2.3(11)	0.01(8)	0.82(13)	4.6(1)	0.17(21)	0.095(18)

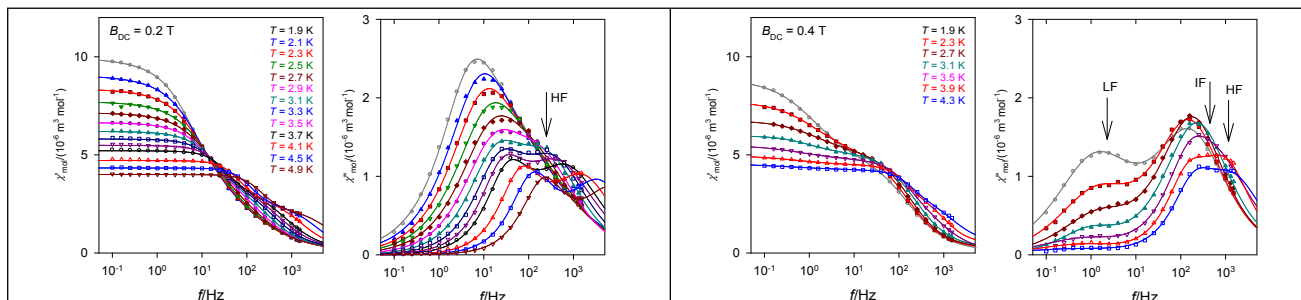


Figure S8. AC susceptibility data for **1**.

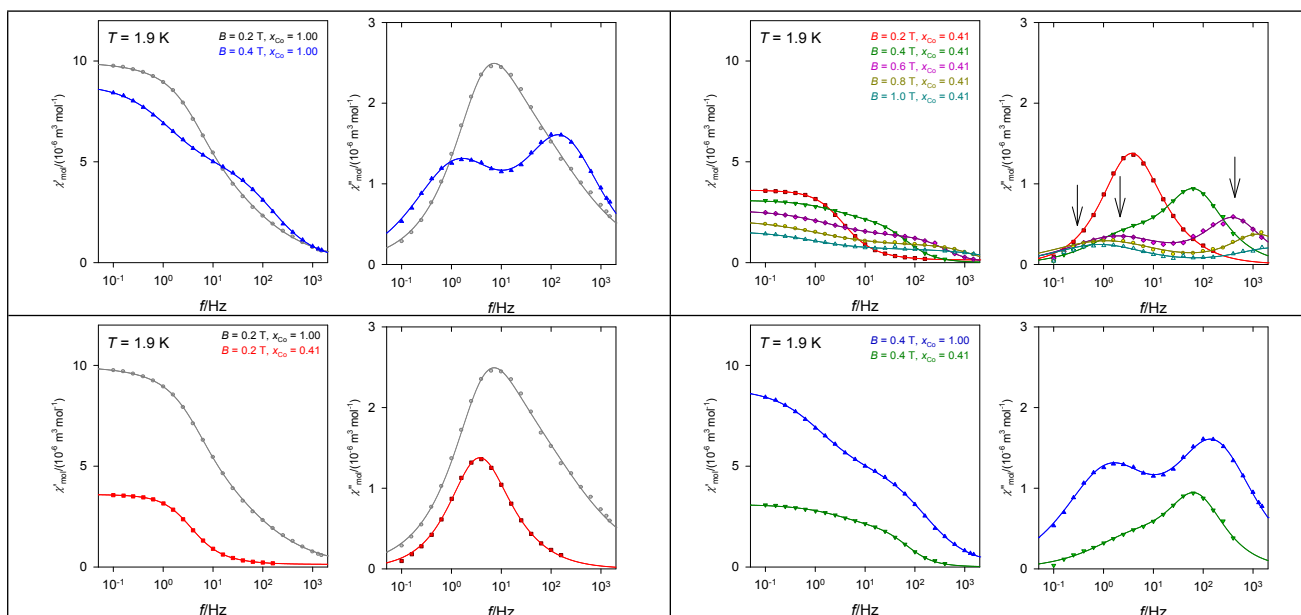


Figure S9. Comparison of the AC susceptibility data for the pure Co and Co:Zn complexes. Lines – fitted. Arrows indicate area of the individual relaxation modes.

Table S6. Results of the fitting procedure for AC susceptibility components of **1** and **1b** at $T = 1.9$ K. ^a

Sample	B/T	$R(\chi'')$ /%	$R(\chi''')$ /%	χ_S	χ_{LF}	α_{LF}	τ_{LF} / 10^{-3} s	f_{LF} / s^{-1}	x_{LF}	χ_{HF}	α_{HF}	τ_{HF} / 10^{-3} s
1 , gray	0.2	0.5	1.7	0	4.88(69)	0.21(3)	29.4(15)	5.5	0.49	9.93(3)	0.47(1)	2.57(81)
1b , red	0.2	0.3	1.9	0.13(3)	3.37(33)	0.12(1)	44.1(21)	3.6	0.93	3.60(1)	0.23(33)	5.8(89)
1 , blue	0.4	0.5	1.5	0.08(3)	4.17(12)	0.33(1)	131(4)	1.2	0.47	8.87(3)	0.28(1)	0.96(2)
1b , green	0.4	0.8	2.7	0	1.05(9)	0.29(4)	57.2(79)	2.8	0.34	3.09(2)	0.12(1)	2.33(8)
1b , violet	0.6	1.1	6.9	0	1.33(6)	0.39(3)	90.2(67)	1.8	0.51	2.60(3)	0.10(2)	0.40(1)
1b , yellow	0.8	1.2	15	0	1.27(8)	0.45(4)	147(18)	1.1	0.60	2.13(5)	0.11(5)	0.13(1)
1b , cyan	1.0	3.0	16	0	0.90(7)	0.37(5)	192(25)	0.83	0.58	1.56(5)	0.29(8)	0.056(8)

^a **1b** = $C_{28}H_{24}Co_{0.41}N_6O_{16}Zn_{0.59}$; **1** = $C_{28}H_{24}CoN_6O_{16}$; f_{LF} – frequency when χ'' is maximal, $f_{LF} = 1/(2\pi\tau_{LF})$; susceptibility components in units of $10^{-6} m^3 mol^{-1}$ [SI].

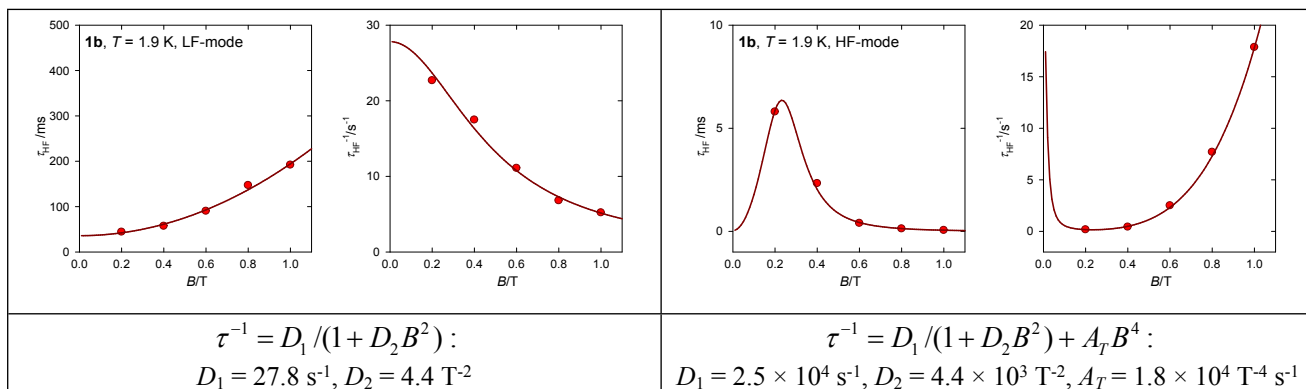


Figure S10. Field dependence of the relaxation time for **1b** = C₂₈H₂₄Co_{0.41}N₆O₁₆Zn_{0.59}.