Electronic supplementary information (ESI)

ESI.1. Synthesis and characterization of *cis*-[Co(hfac)$_2$·(H$_2$O)$_2$] (I) and *cis*-[Co$_{0.02}$Zn$_{0.98}$(hfac)$_2$(H$_2$O)$_2$]

All chemicals were purchased from commercial sources and used without further purification. The FT-IR spectra of microcrystalline powders were recorded on Perkin-Elmer Spectrum 100 spectrometer. The powder XRD patterns were recorded at room temperature on an ARL X'TRA X-ray diffractometer. Synthesis of the complex *cis*-[Co(hfac)$_2$·(H$_2$O)$_2$] (hfac = hexafluoroacetylacetonate) was based on the known literature procedure.[1,2] Anal. Calc. For $C_{10}H_6O_6F_{12}Co_1$: C, 23.59; H, 1.19; F, 44.78; Co, 11.58%; Found: C, 23.16; H, 1.26; F, 40.98; Co, 10.85%. Elemental analysis of this complex was performed by pyrolysis. As a result not all F atoms were burned, and cobalt fluoride was formed, which led to the underestimated percentage of fluorine and cobalt. IR (cm^{-1}): 3466 m, 1641 s, 1610 m, 1564 m, 1537 m, 1484 s, 1346 w, 1256 s, 1212 s, 1141 s, 1095 m, 806 s, 746 w. Magnetically diluted sample

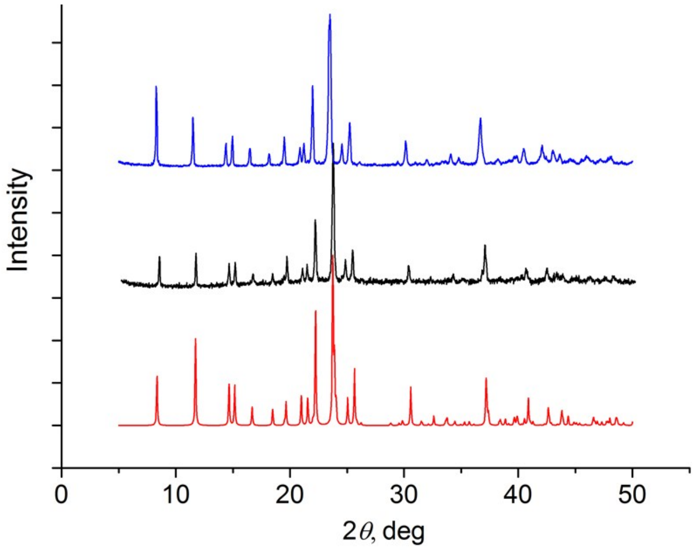


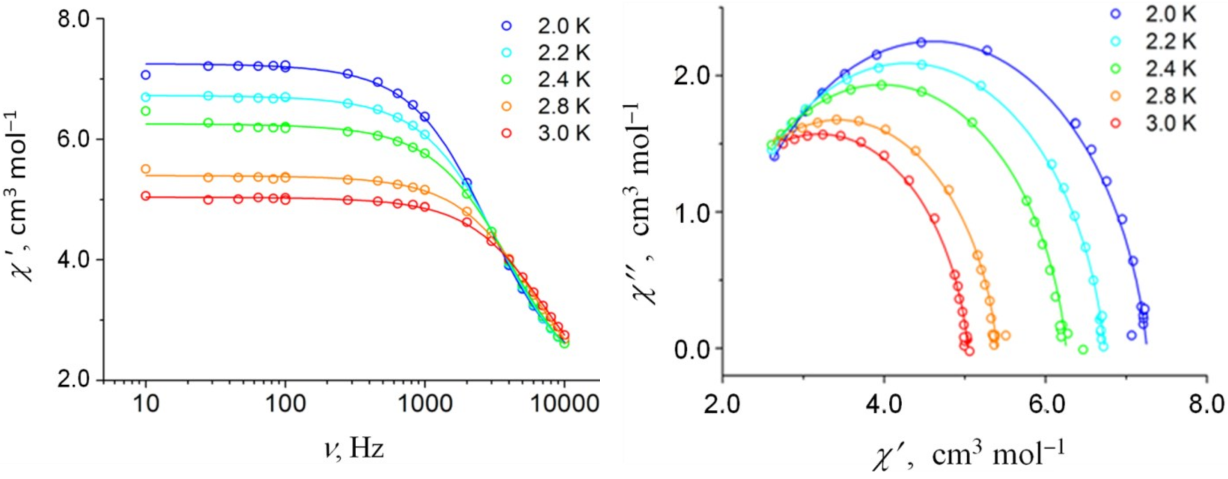
Figure ESI.1. Powder X-ray diffraction pattern of polycrystalline samples of complexes: experimental for complex **I** (black), experimental for magnetically diluted sample *cis*-[Co$_{0.02}$Zn$_{0.98}$(hfac)$_2$(H$_2$O)$_2$] (blue), and calculated from single crystal data for complex **I** (CSD code *FEYFEV*) (red).

cis-[Co$_{0.02}$Zn$_{0.98}$(hfac)$_2$(H$_2$O)$_2$] was prepared by cocrystallization of complex **I** and its isostructural Zn analogue with ratio Co/Zn = 1 : 50. Anal. Calc. for $C_{10}H_6O_6F_{12}Co_{0.02}Zn_{0.98}$: C, 23.59; H, 1.19;

Found: C, 23.10; H, 1.14. IR (cm^{-1}) for $C_{10}H_6O_6F_{12}Co_{0.02}Zn_{0.98}$: 3461 m, 1646 s, 1615 m, 1567 m, 1540 m, 1460 s, 1349 w, 1256 s, 1222 s, 1205 s, 1149 s, 1093 m, 808 s, 747 w. The powder XRD measurements showed that samples are monophase crystalline materials (Fig. ESI.1.).

ESI. 2. Dynamic susceptibility

The frequency dependences of in phase (χ') and out of phase (χ'') components of the AC magnetic susceptibility measured at B = 0.1 T DC field and different temperatures are shown in Figure ESI.2a and Figure.4a of the main text, respectively. The Argand (Cole−Cole) plot is shown in Fig.ESI.2b.



(a) (b)

Fig. ESI.2. Frequency dependence of the in-phase (a) AC susceptibility, and Argand (Cole−Cole) plot (b) of complex **I** under 0.1 T DC field and temperature ranging from 2 to 3 K. Empty circles- experimental data, solid lines- fit to the generalized Debye model with the set of parameters listed in Table ESI.3.

These dependences were fit to the generalized Debye model [3] within which the in phase (χ') and out of phase (χ'') components of the AC magnetic susceptibility are defined according to the empirical low:

$$\chi'(\nu) = \chi_S + \Delta\chi_T \frac{1+(2\pi\nu\tau)^{1-\alpha}\sin(\pi\alpha/2)}{1+2(2\pi\nu\tau)^{1-\alpha}\sin(\pi\alpha/2)+(2\pi\nu\tau)^{2-2\alpha}},$$

$$\chi''(\nu) = \Delta\chi_T \frac{(2\pi\nu\tau)^{1-\alpha}\cos(\pi\alpha/2)}{1+2(2\pi\nu\tau)^{1-\alpha}\sin(\pi\alpha/2)+(2\pi\nu\tau)^{2-2\alpha}},$$

$$\Delta\chi_T = \chi_T - \chi_S,$$

where ν is the frequency of the applied AC field, χ_T and χ_S are the isothermal and adiabatic susceptibilities, respectively, τ is the relaxation time, and α is the dispersion coefficient showing the distribution of the relaxation times. The found best-fit values of the parameters χ_S, $\Delta\chi_T$, τ and α are listed in Table ESI.3.

Table ESI.2.Best fit values of the parameters of the generalized Debye model for complex **I** under DC field of 0.1 T.

T, K	χ_S, cm^3 mol^{-1}	$\Delta\chi_T$, cm^3 mol^{-1}	τ, s	α
2.0	1.95(3)	5.31(4)	5.65(7)E-05	0.104(7)
2.2	1.83(2)	4.90(2)	4.74(3)E-05	0.100(3)
2.4	1.69(4)	4.56(5)	3.95(6)E-05	0.104(8)
2.8	1.47(2)	3.92(2)	2.68(3)E-05	0.100
3.0	1.36(2)	3.68(2)	2.19(2)E-05	0.100

ESI. 3. Computational details

The calculation of the energies of the low-lying magnetic d-orbitals of **I** has been carried out with the aid of spin averaged Hartree-Fock (SAHF) procedure [4] based on restricted open-shell Hartree–Fock (ROHF) method. The SAHF calculation was performed with the polarized triple-ζ-quality basis set def2-TZVP [5] using ORCA program package (version 3.0.3).[6] Table ESI.3 allows to compare the energies of the low-lying magnetic d-orbitals of **I** calculated using SAHF and SA-CASSCF/NEVPT2 methods. It is seen that SA-CASSCF/NEVPT2 method gives for the parameter Δ_{ax} the value that is close to that obtained in the framework of SAHF approach, but the rhombic CF parameter obtained with SA-CASSCF/NEVPT2 proves to be significantly lower than that found with SAHF, and it is apparently incompatible with the EPR data.

Table ESI.3. Energies (eV) of the five low-lying magnetic d-orbitals of **I** calculated using two different methods.

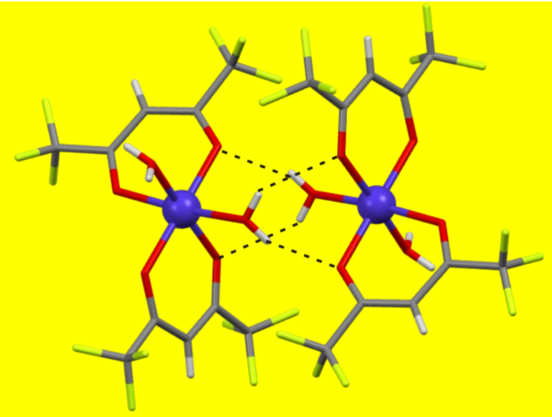
Method	SAHF	SA-CASSCF/NEVPT2
	-17.1061	-9.3989
	-17.0526	-9.3338
	-17.0357	-9.3329
	-16.4034	-8.4981
	-16.1845	-8.4694
Δ_{ax}, cm^{-1}	-499.7	-528.7
Δ_{romb}, cm^{-1}	136.3	7.3

Quantum-chemical calculations of the ***g***-tensor based on experimental geometry (CSD code *FEYFEV*) have been performed by the ORCA program.[7] For this purpose, complete active space self-consistent field (CASSCF) and the second-order *N*-electron valence perturbation theory (NEVPT2) [8] (to account for the dynamic correlations) methods have been used. An active space with seven electrons distributed over five cobalt *d* orbitals (CAS(7,5)) has been employed with the def2-TZVP basis set. In the state-average CASSCF procedure, the orbitals have been optimized for the average of 10 quartet (S = 3/2) and 40 doublet (S = 1/2) roots. The ***g*** -tensor has been calculated using quasi-degenerate perturbation theory (QDPT) approach within an individual Kramers doublet.[9] This analysis is valid only for the case of half-integer spin, in particular for systems with well isolated Kramers doublets. This is just the case under consideration in which the EPR spectrum originates from the only lowest Kramers doublet defined within the pseudo spin-1/2 formalism.

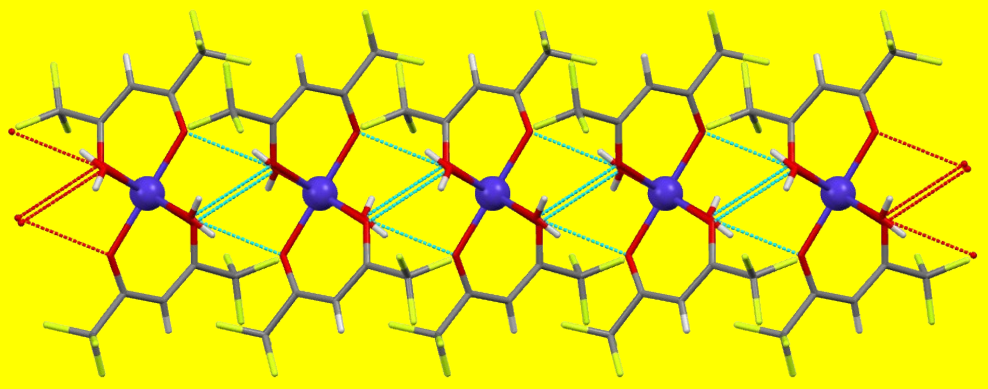
The constant J of the magnetic superexchange between the H-bonded cobalt ions (Fig. ESI.3) has been calculated using the broken-symmetry (BS) density functional theory (DFT) approach proposed in Refs. [10, 11] and implemented in ORCA program. Calculations have been performed with a B3LYP/TZV level of theory using the expression

$$J = \frac{E_{BS} - E_{\mathrm{HS}}}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}},$$

derived in Ref. [9] from the analysis of the Heisenberg—Dirac—van Vleck spin Hamiltonian $\hat{H}_{ex} = -2J\, \hat{\boldsymbol{S}}_A \hat{\boldsymbol{S}}_B$. In this expression E_{BS} and E_{HS} are the total energies of the BS and high-spin



(a)



(b)

Figure ESI. 3. Hydrogen O-H…O bonds mediating exchange coupling between the nearest neighboring Co(II)-complexes (a), and formation of 1D chain composed of cobalt complexes (b).

(S=3 –state for dimer) states, respectively, $<S^2>_{BS}$ and $<S^2>_{HS}$ are the corresponding average values of the square spin operator.

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