

## Single molecule magnet behaviour in a square planar $S = 1/2$ Co(II) complex and spin-state assignment of multiple relaxation modes

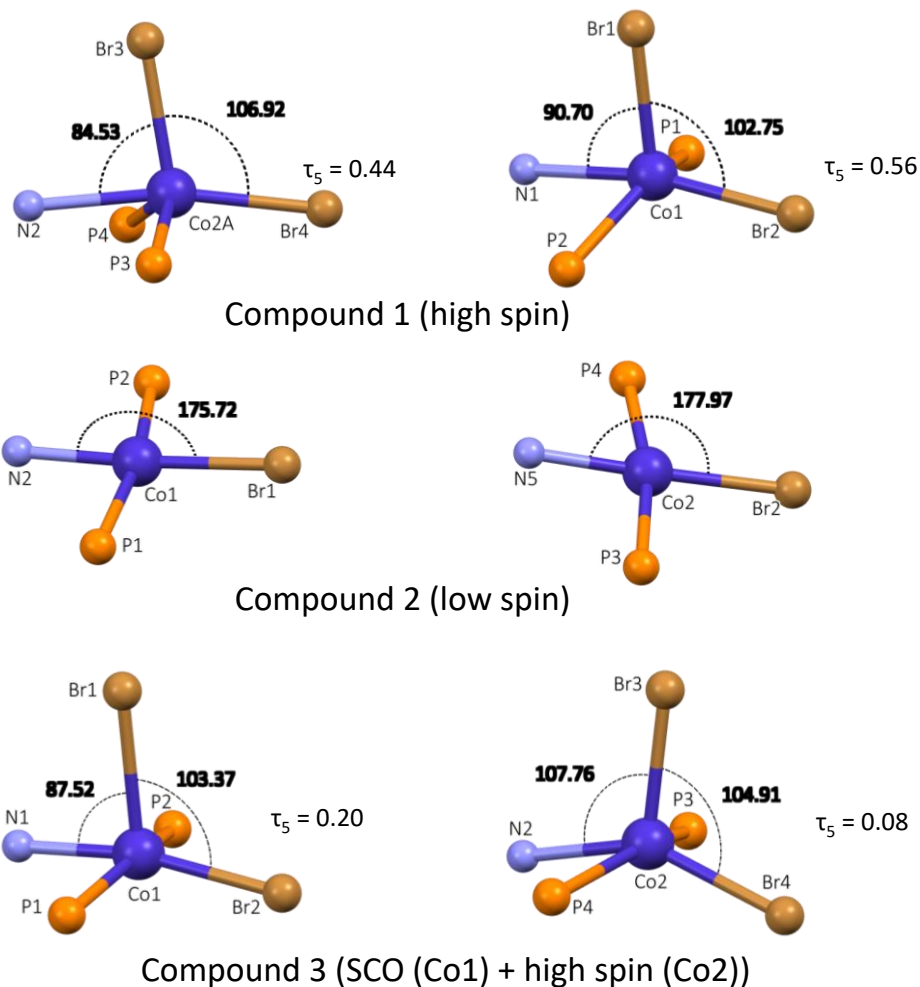
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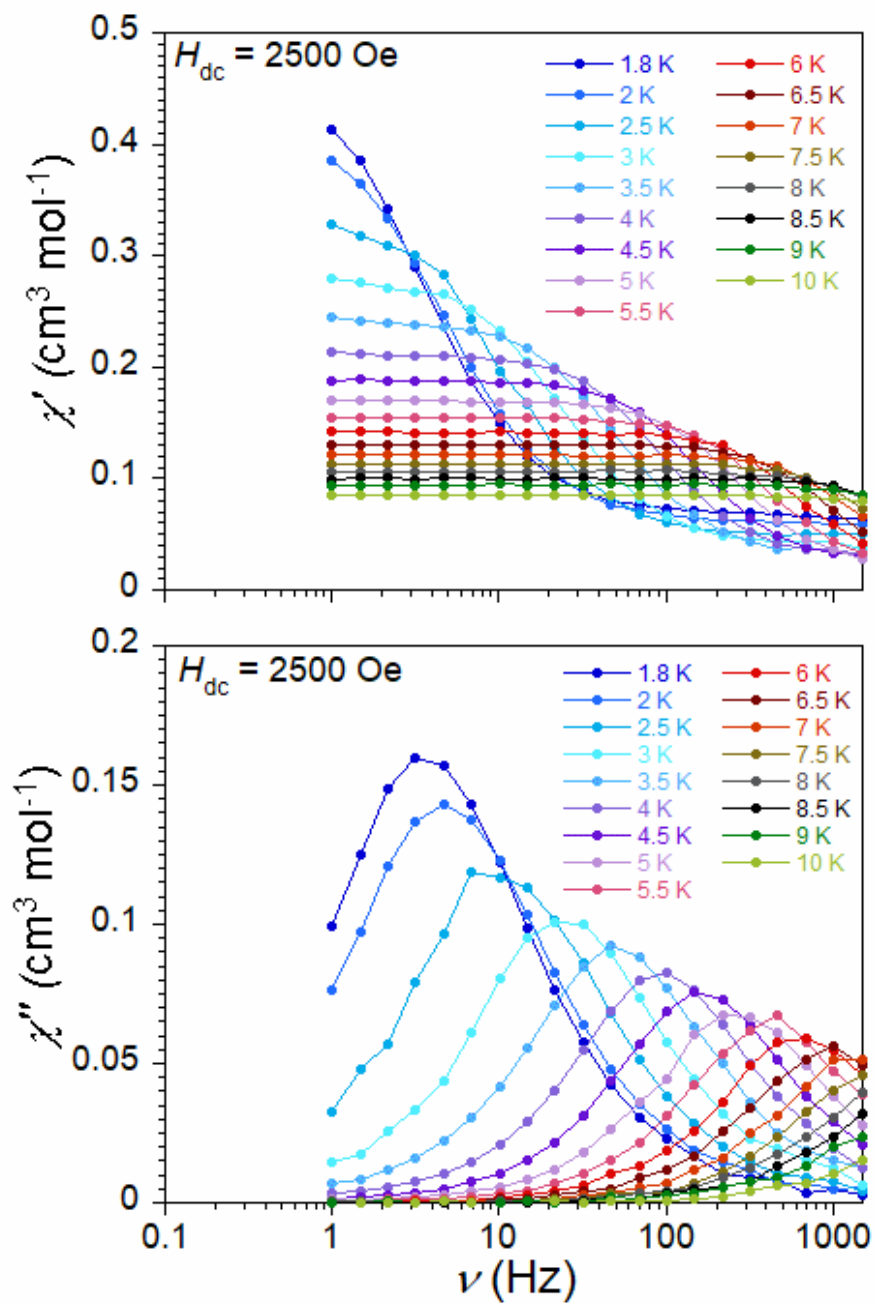
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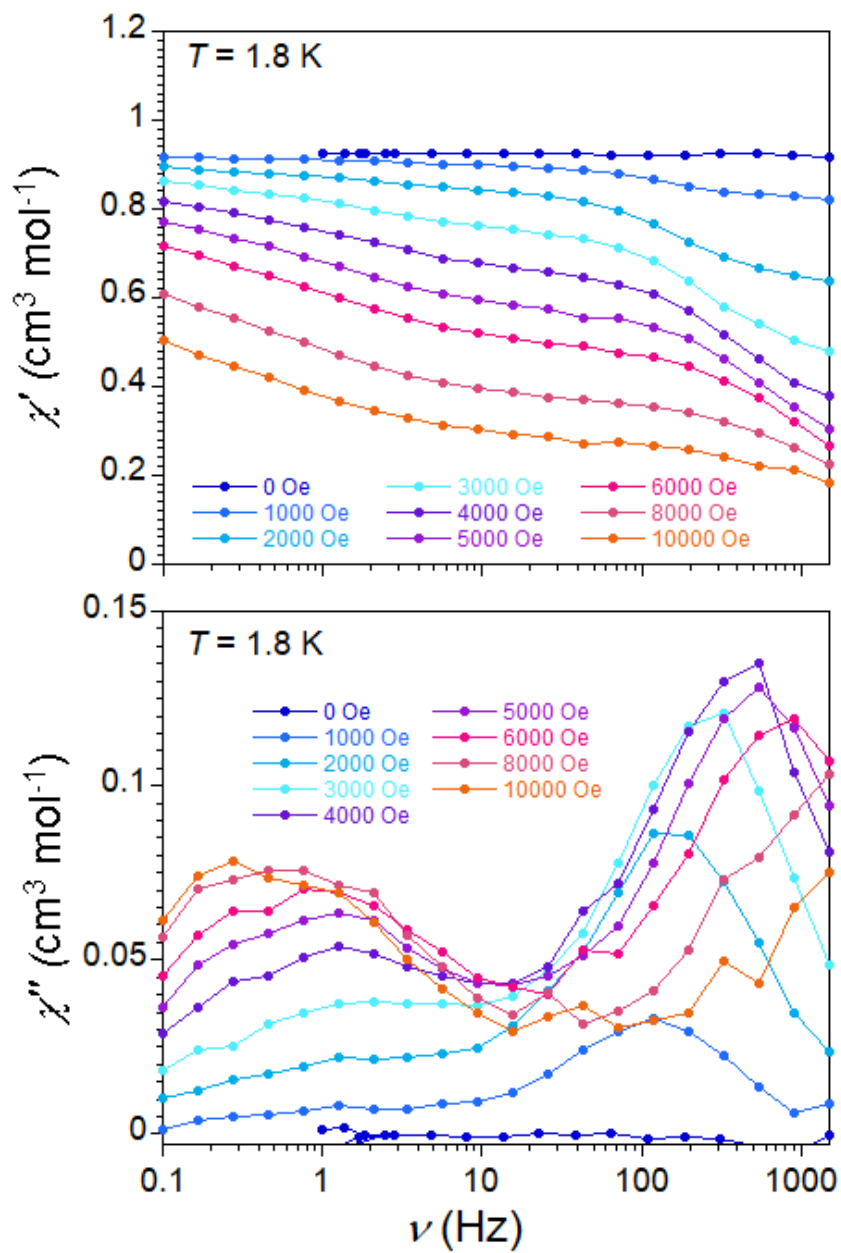
**Fig. S1** The local molecular geometry of the three sets of Co(II) complexes. The *t*-butyl groups, solvent molecules and the charge-balancing anions are not shown. The quantity  $\tau_5$  is defined as the value of  $(\beta - \alpha)/60$ , where  $\beta$  is the largest ligand-metal-ligand bond angle and  $\alpha$  is the second largest. In compound **3** we expect that the Co(1) center ( $\tau_5 = 0.20$ ), which has bond distances similar to the square planar **2**·EtOH, undergoes spin-crossover from high-spin  $S = 3/2$  to low-spin  $S = 1/2$ .<sup>[ESI1]</sup>



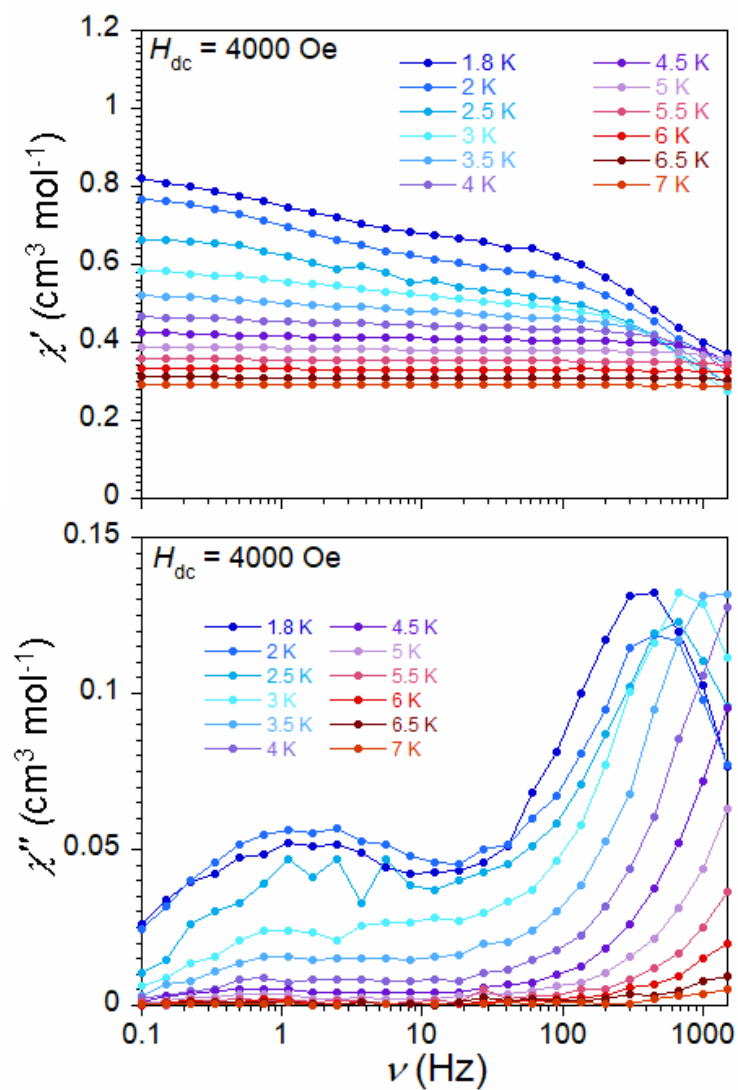
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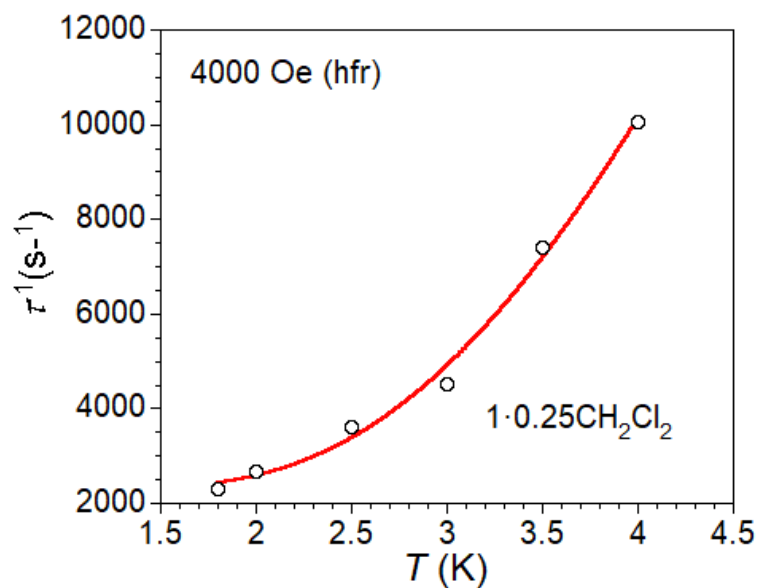
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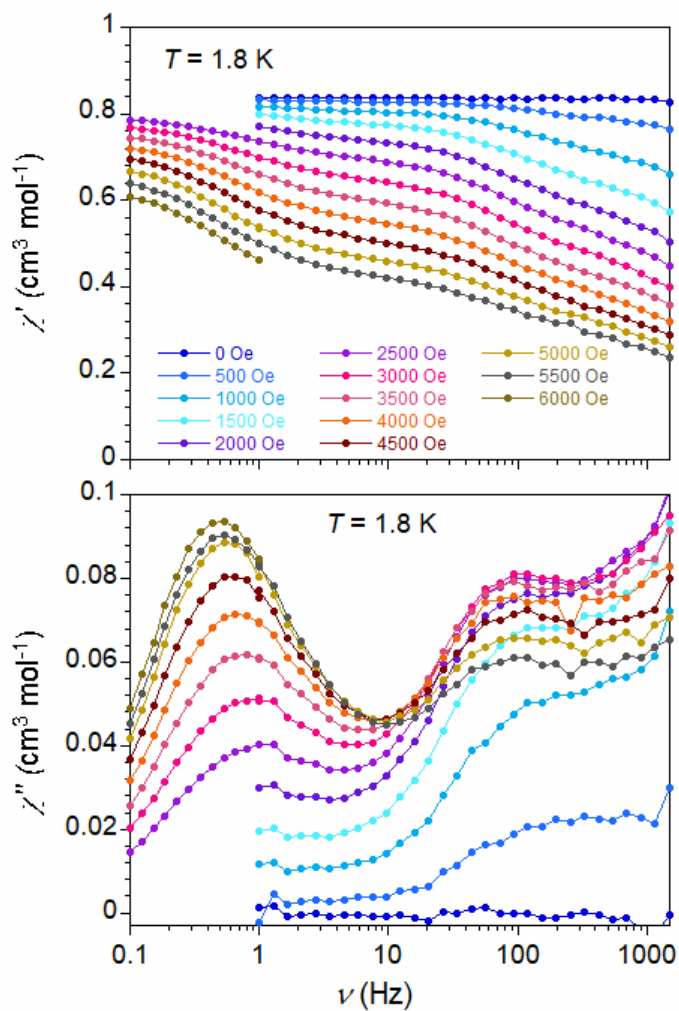
**Fig. S4** Frequency dependencies of in-phase ( $\chi'$ , top) and out-of-phase ( $\chi''$ , bottom) parts of the ac magnetic susceptibility of  $1 \cdot 0.25\text{CH}_2\text{Cl}_2$  acquired with a 4 Oe oscillating ac field at 1.8 K at different applied dc fields up to 10000 Oe.



**Fig. S5** Temperature dependencies of in-phase ( $\chi'$ , top) and out-of-phase ( $\chi''$ , bottom) parts of the ac magnetic susceptibility for  $1\cdot 0.25\text{CH}_2\text{Cl}_2$ ; data acquired at 4000 Oe applied dc field and 4 Oe oscillating ac field at different temperatures between 1.8 K and 7 K.

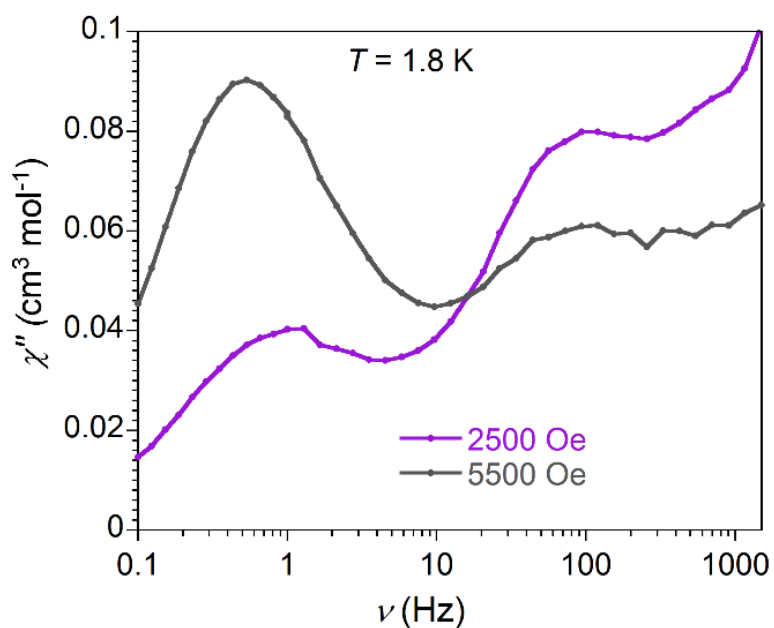


**Fig. S6** Best fit of the temperature-dependent relaxation time of the 1 hfr mode of compound  $1 \cdot 0.25\text{CH}_2\text{Cl}_2$  to the equation  $\tau_{1\text{hfr}}^{-1}(T) = \tau_{\text{QTM}}^{-1} + \tau_0^{-1} \exp(-U_{\text{eff}}/k_B T)$ , where the  $\tau_{\text{QTM}}$  is relaxation time of QTM,  $\tau_0$  is the pre-exponential constant and  $U_{\text{eff}}$  is the energy needed to reverse the magnetization according to the Orbach relaxation process. The best fit provides parameters  $\tau_{\text{QTM}} = 4.36 \times 10^{-4}$  s,  $\tau_0 = 4.72 \times 10^{-6}$  s and  $U_{\text{eff}} = 9.17$  cm $^{-1}$ .

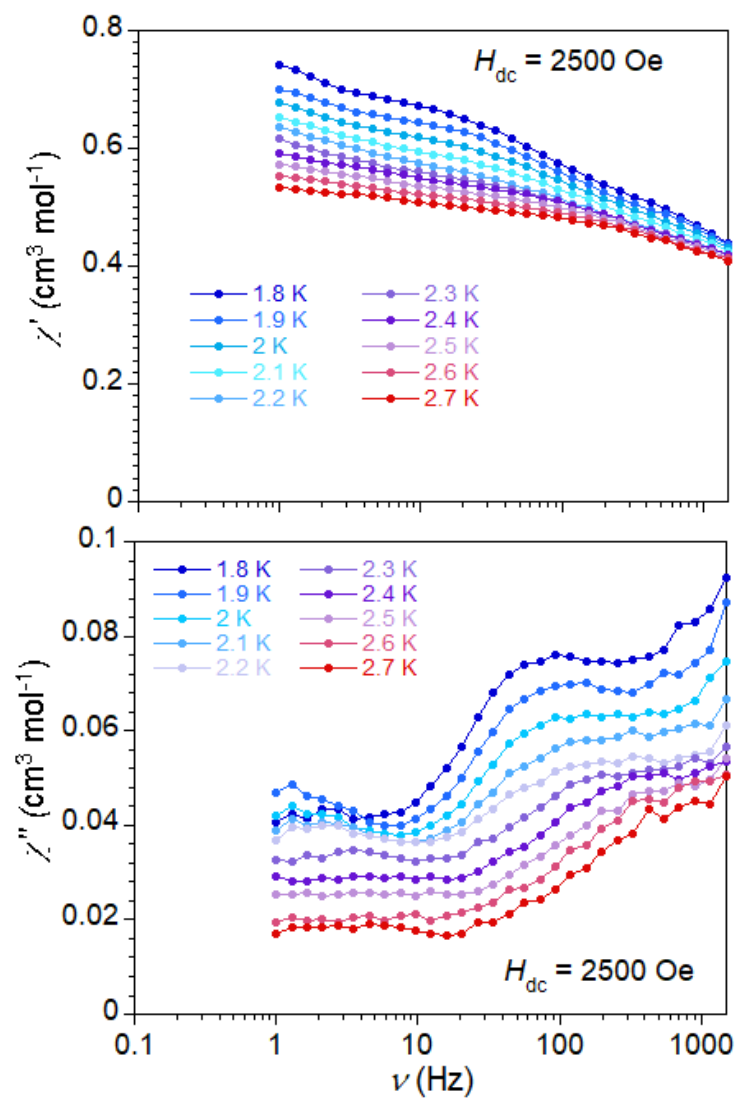


**Fig. S7** The frequency dependencies of in-phase ( $\chi'$ , top) and out-of-phase ( $\chi''$ , bottom) parts of the ac magnetic susceptibility of **3** acquired with a 4 Oe oscillating ac field at 1.8 K at different applied dc fields up to 6000 Oe.

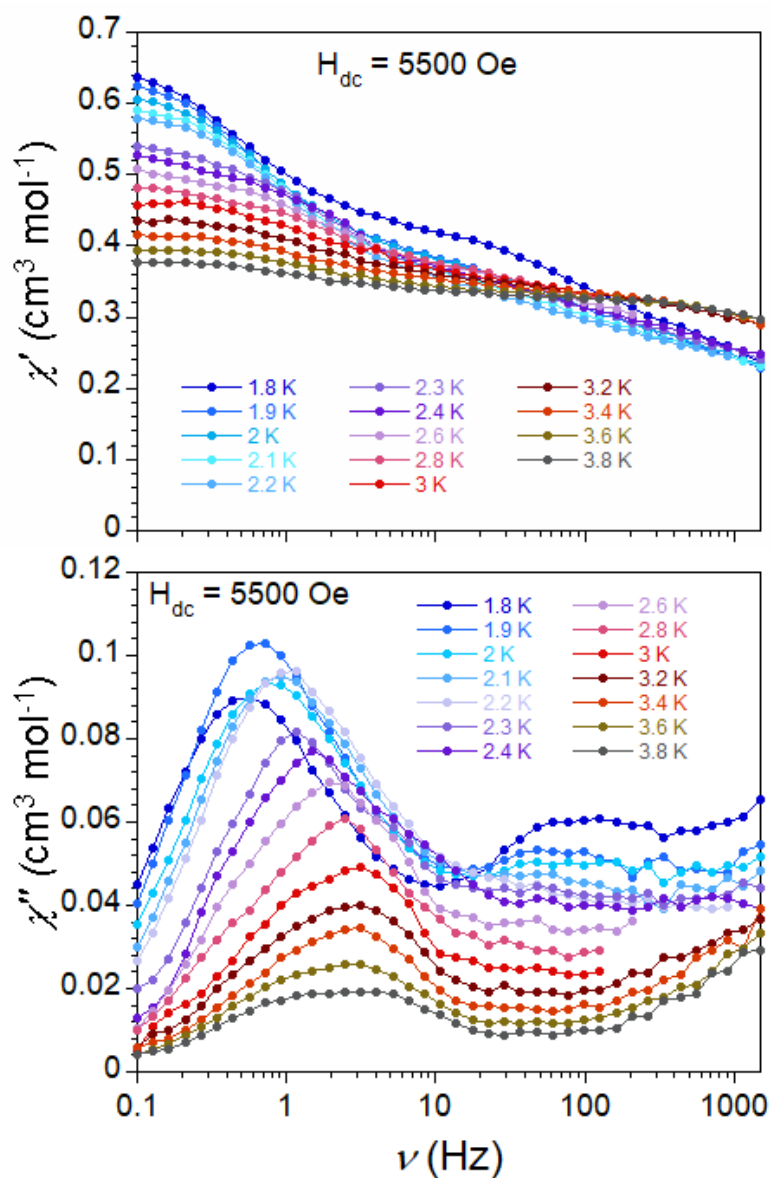




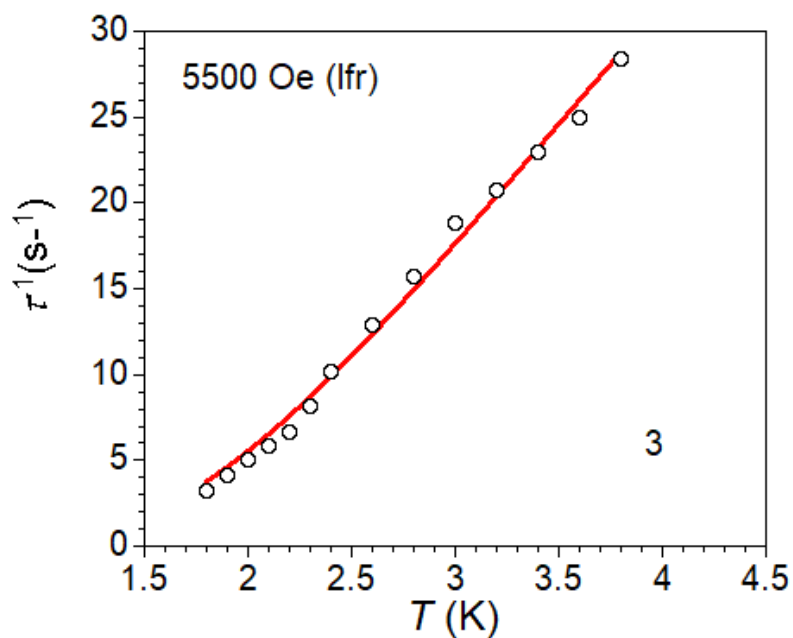
**Fig. S8** Frequency dependence out-of-phase ( $\chi''$ ) ac magnetic susceptibility of **3** at 1.8 K at 2500 Oe and 5500 Oe with a 4 Oe oscillating ac field (data same as shown in Figure S7). At the larger dc field the low frequency relaxation (lfr) increases in intensity and the medium frequency relaxation (mfr) mode decreases and/or overlaps with frequencies associated with high frequency relaxation (hfr) pathway.



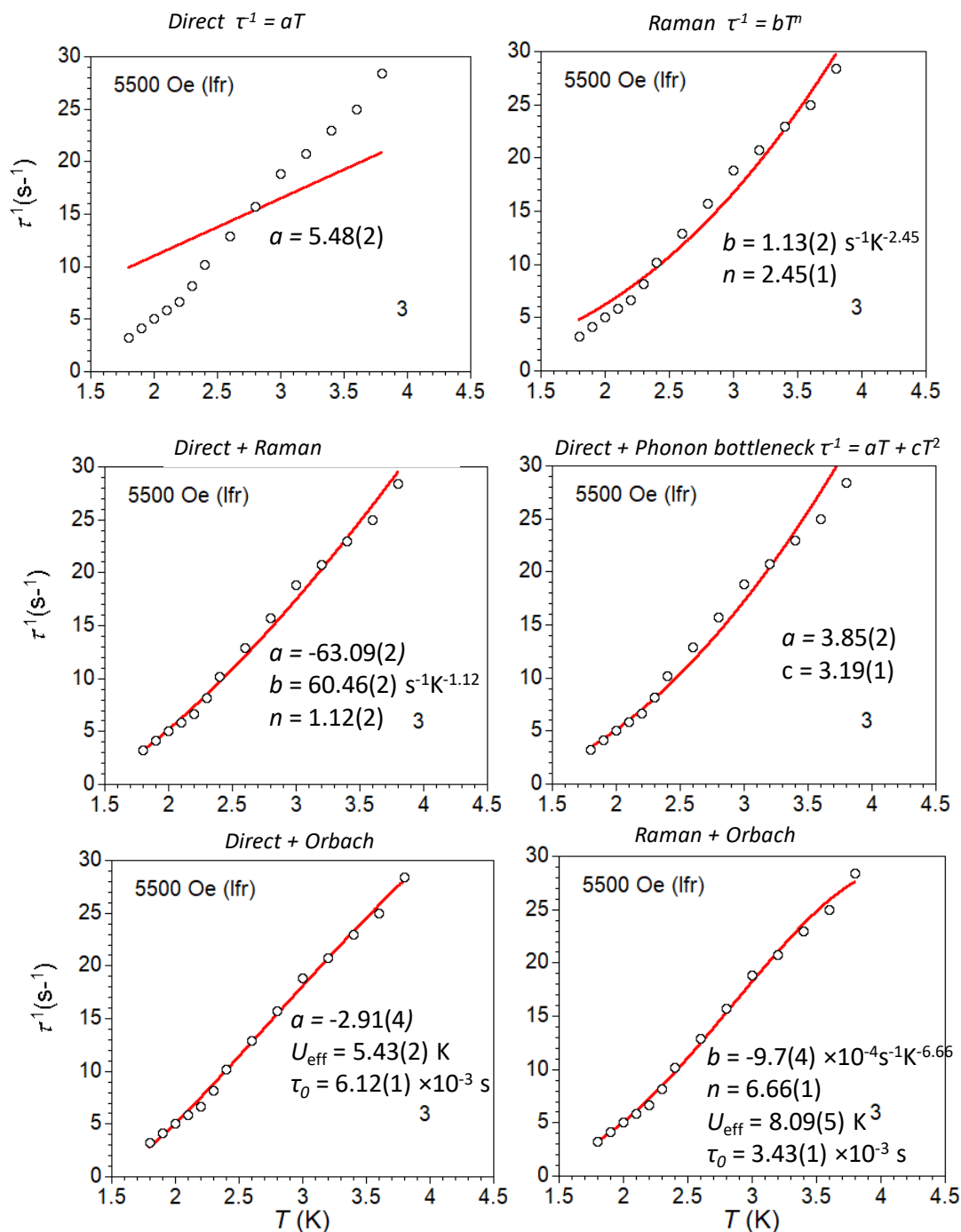
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**Fig. S10** Temperature dependencies of in-phase ( $\chi'$ , top) and out-of-phase ( $\chi''$ , bottom) parts of the ac magnetic susceptibility for **3**; data acquired at 5500 Oe applied dc field and 4 Oe oscillating ac field at different temperatures between 1.8 K and 3.8 K.



**Fig. S11** Best fit of the temperature dependent relaxation time of the **3**:lfr mode of compound **3** to the equation  $\tau_{3:lfr}(T)^{-1} = \tau_0^{-1} \exp(-U_{\text{eff}}/k_B T)$ , where the  $\tau_0$  is the pre-exponential constant and  $U_{\text{eff}}$  is the energy needed to reverse the magnetization according to the Orbach relaxation process. The best fit provides parameters  $\tau_0 = 5.51 \times 10^{-3}$  s and  $U_{\text{eff}} = 4.87$  cm<sup>-1</sup>.



**Fig. S12** Attempts to fit the temperature dependence of the relaxation time of  $3^1\text{Irf}$  relaxation mode with various combinations of spin-lattice relaxation mechanism.

## References

[ESI1] D. W. Shaffer, I. Bhowmick, A. L. Rheingold, C. Tsay, B. N. Livesay, M. P. Shores, J. Y. Yang, *Dalton Trans.*, 2016, **45**, 17910-17917.