Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for:

Slow Relaxation of Magnetization in a Bis-*mer*-Tridentate Octahedral Co(II) Complex

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IR and NMR data

Figure S1 IR spectra for [Co(Himap)$_2$] **1** (top) and [Co(Himap)$_2$]NO$_3$·MeOH **2** (bottom).

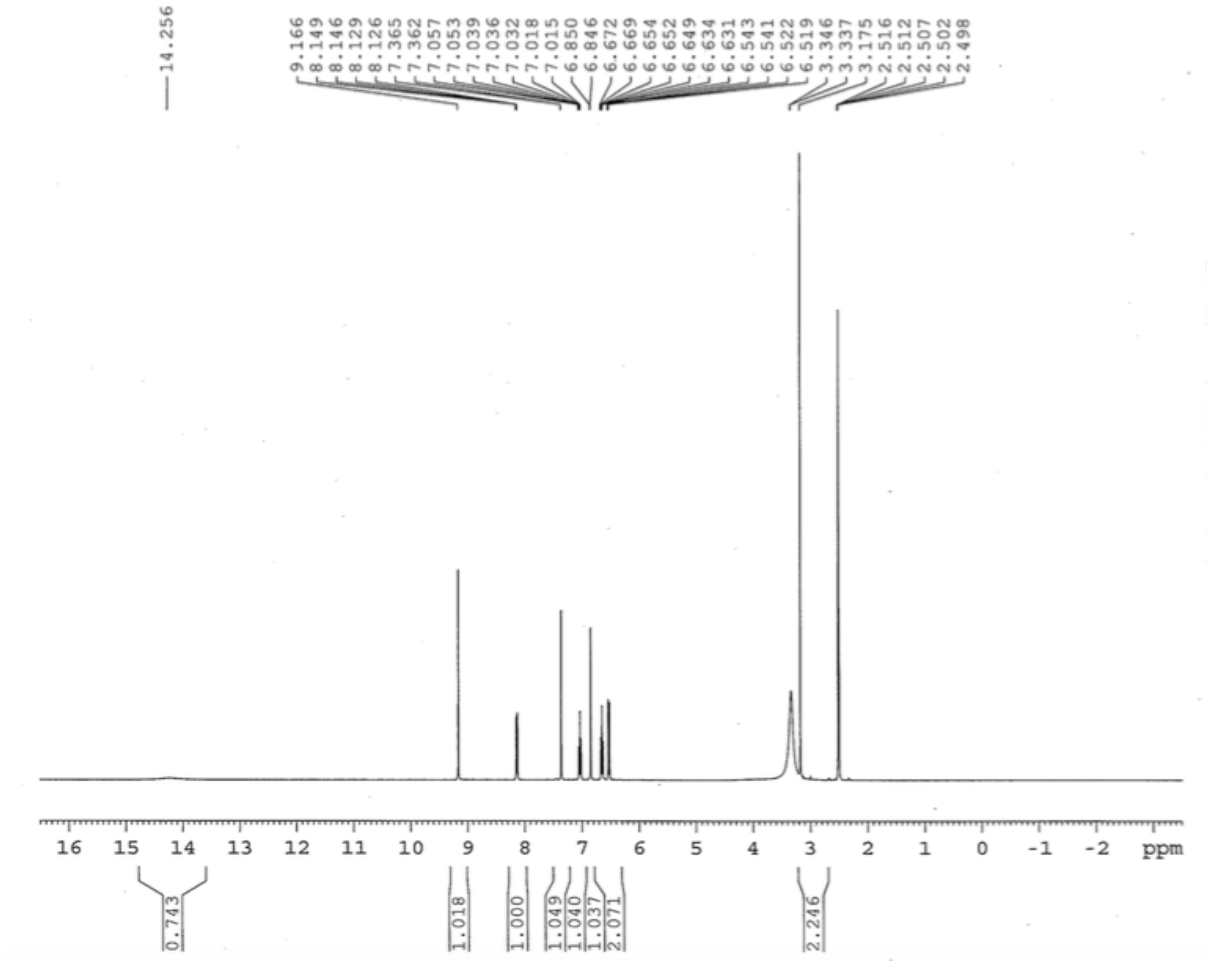

Figure S2 ^{1}H NMR spectrum of $[Co(Himap)_2]NO_3 \cdot MeOH$ in d^6-DMSO at 298 K.

Magnetic studies

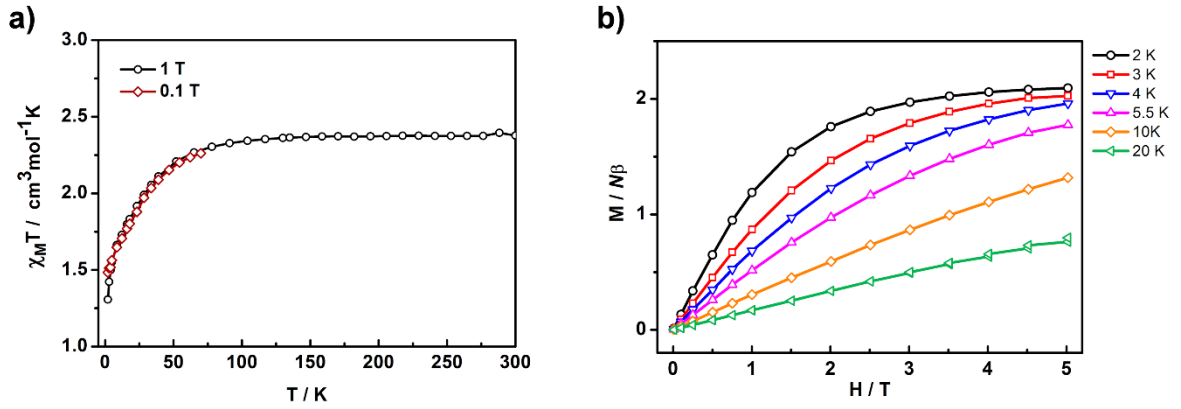

Figure S3 Experimental plot of a) $\chi_M T$ vs. T at H = 1 T and 0.1 T and b) M vs. H at the temperatures shown for **1**.

The magnetic susceptibility and magnetization values were fitted using ORCA or MOLCAS at different external fields and temperatures. In the $\chi_M T$ vs. T simulations, experimental and calculated values for all three methods are shown in Figure S4. In the ORCA calculations different external fields were applied but the molar susceptibility shows no dependency on this factor; therefore, only the curves at a field of 0 T are shown. It is noteworthy that all the calculations produce $\chi_M T$ values that are too large, with the ORCA/NEVPT2 method closest to the experimental results.

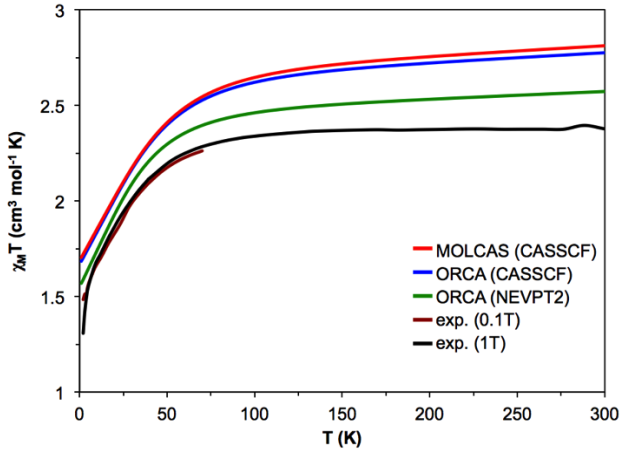

Figure S4 Experimental and simulated $\chi_M T$ vs. T curves.

The magnetization has been simulated at 2, 3, 4, 5.5, 10 and 20 K within a field range between 0 and 5 T (Figure S5). Only the MOLCAS/CASSCF and ORCA/NEVPT2 results are shown (those obtained with ORCA/CASSCF are very similar to the latter). The results obtained with MOLCAS show a poor fit and the magnetization values are always underestimated. In contrast, the magnetization values obtained with ORCA show a much better agreement with the experimental data.

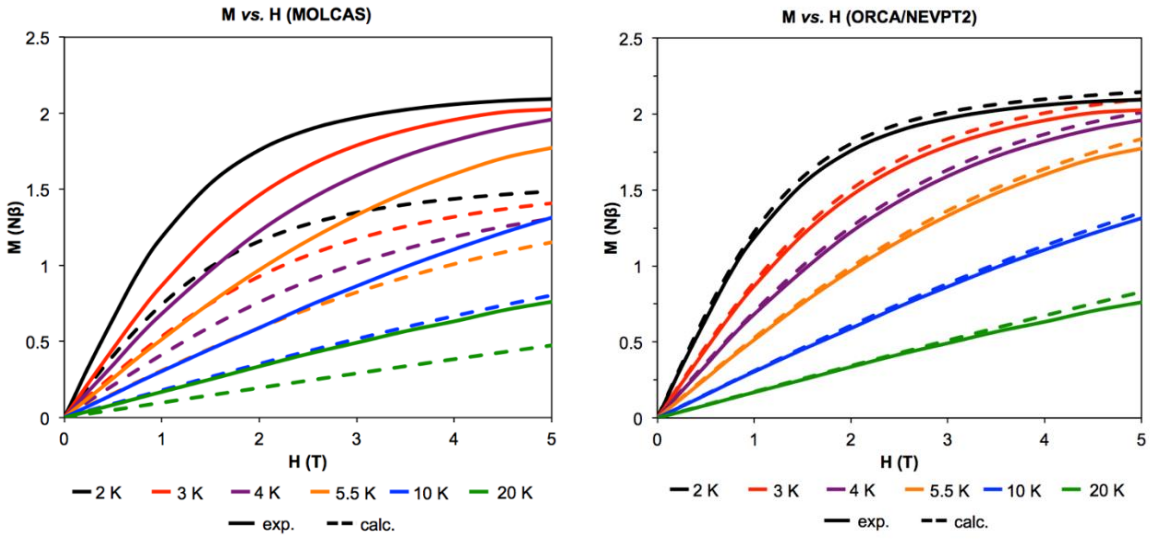

Figure S5 Experimental and simulated magnetization values obtained with MOLCAS/CASSCF (left) and ORCA/NEVPT2 (right).

The fits of the *ac* magnetic data also generate relaxation time τ values that when plotted as ln(τ) against 1/T gave a curved plot (Figure S6). The curve was fitted to a spin-lattice relaxation rate expression that included Raman, Orbach and temperature independent quantum tunneling terms, respectively.

$$\tau^{-1} = CT^{n} + \tau_o^{-1}\exp(-U_{eff}/kT) + B \quad (1)$$

Details of the *B* term are given in a recent Co(II) SIM paper by Diaz-Torres *et al*.[1] That work also included a direct relaxation term *A'T*. The best fits here, for **1**, employed *n* of 2.8 and 2.9 with *n* = 2.9 yielding U_{eff} = 14 K, *C* = 421 $K^{-2.9}$ s^{-1}, τ_0 = 5 x 10^{-4} s and *B* = -76 s^{-1}. The *B* and *C* terms are sensitive to small changes in *n*, and *B* should be positive. As indicated in the main paper, the Orbach mechanism does not contribute greatly to the spin relaxation in **1** and is included here in the interests of completeness.

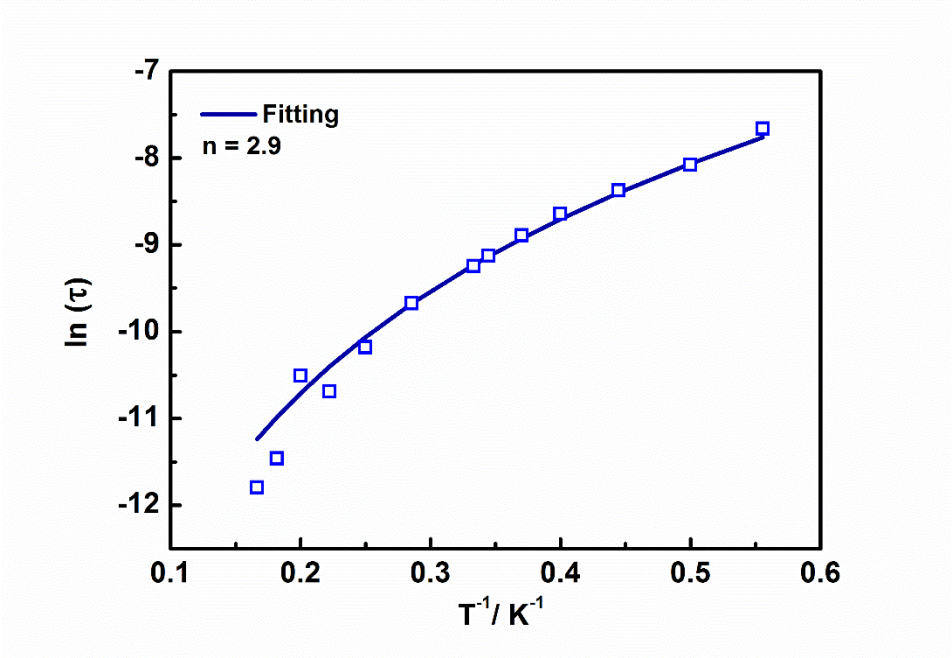

Figure S6 Relaxation time vs. 1/*T* plot and best fit as described in the text, with n = 2.9, for complex **1** using *ac* χ_M'' data in a *dc* field of 0.2 T.

References

1 R. Díaz-Torres, M. Menelaou, O. Roubeau, A. Sorrenti, G. Brandariz-de-Pedro, E. C. Sañudo, S. J. Teat, J. Fraxedas, E. Ruiz and N. Aliaga-Alcalde, *Chem. Sci.*, 2016, **7**, 2793–2803.