Supplementary Information for:

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

Darunee Sertphon,1 Keith S. Murray,2 Wasinee Phonsri,2 Jesús Jover,3 Eliseo Ruiz,3 Shane G. Telfer,4 Adil Alkaş,4 Phimphaka Harding1 and David J. Harding1*

1Functional Materials and Nanotechnology Centre of Excellence, Walailak University, Thasala, Nakhon Si Thammarat, 80160, Thailand
2School of Chemistry, Monash University, Clayton, Victoria, 3800, Australia
3Departament de Química Inorgànica and Institut de Química Teòrica i Computacional, Universitat de Barcelona, Diagonal 645, E-08028 Barcelona, Spain
4MacDiarmid Institute for Advanced Materials and Nanotechnology, Institute of Fundamental Sciences, Massey University, Palmerston North, New Zealand
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$_3$·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 $\tau$ values that when plotted as $\ln(\tau)$ 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.

$$
\tau^{-1} = C T^n + \tau_0^{-1} \exp(-U_{eff}/kT) + B
$$  \hspace{1cm} (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$^{-1}$, $\tau_0 = 5 \times 10^{-4}$ 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 $\chi_M$ data in a dc field of 0.2 T.

References