Supplementary Material (ESI) for Chemical Communications

Supplementary information

First trinuclear paramagnetic transition metal complexes with redox active ligands derived from TTF: $Co_2M(PhCOO)_6(TTF\text{-}CH{=}CH\text{-}py)_2{\cdot}2CH_3CN$, $M = Co^{II}, Mn^{II}$

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The spin Hamiltonian of **2** is the following

$$H = -J\,\boldsymbol{S_{Co}}\cdot\boldsymbol{S_{Mn}} + g_{Co}\beta\boldsymbol{H}\cdot\boldsymbol{S_{Co}} + g_{Mn}\beta\boldsymbol{H}\cdot\boldsymbol{S_{Mn}} \text{ with } \boldsymbol{S_{Co}} = \boldsymbol{S_{Co_1}} + \boldsymbol{S_{Co_2}}$$

In using the total spin of the system: $\boldsymbol{S} = \boldsymbol{S_{Mn}} + \boldsymbol{S_{Co}}$ the energy levels in zero field are expressed as

$$E(S, S_{Co}) = -\frac{J}{2}\left(S(S+1) - S_{Co}(S_{Co}+1) - S_{Mn}(S_{Mn}+1)\right)$$

S_{Co} varies by integer values from 0 to 3 and S by integer values, for a given value of S_{Co}, from $|S_{Co} - 5/2|$ to $S_{Co} + 5/2$ with $S_{Co_1} = S_{Co_2} = 3/2$ and $S_{Mn} = 5/2$.

The Zeeman factors of each spin state with the energy $E(S, S_{Co})$ are related to the local Zeeman factors g_{Co} and g_{Mn} through:

$$g(S, S_{Co}) = \frac{g_{Co}\left(S(S+1) + S_{Co}(S_{Co}+1) - S_{Mn}(S_{Mn}+1)\right)}{2S(S+1)} + \frac{g_{Mn}\left(S(S+1) - S_{Co}(S_{Co}+1) + S_{Mn}(S_{Mn}+1)\right)}{2S(S+1)}$$

The expression of the zero field magnetic susceptibility is obtained with the Van Vleck formula:

$$\chi_M T = \frac{N\beta^2}{3k}\frac{\sum_{S_{Co}=0}^{3}\sum_{S=|S_{Co}-5/2|}^{S_{Co}+5/2} g(S, S_{Co})^2\, S(S+1)(2S+1)\exp\left(\frac{-E(S, S_{Co})}{kT}\right)}{\sum_{S_{Co}=0}^{3}\sum_{S=|S_{Co}-5/2|}^{S_{Co}+5/2}(2S+1)\exp\left(\frac{-E(S, S_{Co})}{kT}\right)}$$

Which finally gives:

$$\chi_M T = \frac{N\beta^2}{3k} \frac{\left\{ \begin{array}{c} \frac{3}{2}\left(\frac{8}{3}g_{Co} - \frac{5}{3}g_{Mn}\right)^2 \exp\left(\frac{-10J}{kT}\right) + 15\left(\frac{14}{15}g_{Co} + \frac{1}{15}g_{Mn}\right)^2 \exp\left(\frac{-17J}{2kT}\right) \\ + \frac{3}{2}\left(-\frac{4}{3}g_{Co} + \frac{7}{3}g_{Mn}\right)^2 \exp\left(\frac{-7J}{kT}\right) + \frac{105}{2}\left(\frac{24}{35}g_{Co} + \frac{11}{35}g_{Mn}\right)^2 \exp\left(\frac{-6J}{kT}\right) \\ + 15\left(\frac{2}{15}g_{Co} + \frac{13}{15}g_{Mn}\right)^2 \exp\left(\frac{-11J}{2kT}\right) + 15\left(-\frac{2}{5}g_{Co} + \frac{7}{5}g_{Mn}\right)^2 \exp\left(\frac{-7J}{2kT}\right) \\ + \frac{105}{2}\left(\frac{12}{35}g_{Co} + \frac{23}{35}g_{Mn}\right)^2 \exp\left(\frac{-3J}{kT}\right) + 126\left(\frac{38}{63}g_{Co} + \frac{25}{63}g_{Mn}\right)^2 \exp\left(\frac{5J}{2kT}\right) \\ + \frac{105}{2}\left(\frac{4}{35}g_{Co} + \frac{31}{35}g_{Mn}\right)^2 \exp\left(\frac{J}{kT}\right) + \frac{105}{2}\left(g_{Mn}\right)^2 \\ + 126\left(\frac{26}{63}g_{Co} + \frac{37}{63}g_{Mn}\right)^2 \exp\left(\frac{J}{2kT}\right) + \frac{495}{2}\left(\frac{56}{99}g_{Co} + \frac{43}{99}g_{Mn}\right)^2 \exp\left(\frac{2J}{kT}\right) \\ + 126\left(\frac{2}{7}g_{Co} + \frac{5}{7}g_{Mn}\right)^2 \exp\left(\frac{5J}{2kT}\right) + \frac{495}{2}\left(\frac{4}{9}g_{Co} + \frac{5}{9}g_{Mn}\right)^2 \exp\left(\frac{5J}{kT}\right) \\ + 429\left(\frac{6}{11}g_{Co} + \frac{5}{11}g_{Mn}\right)^2 \exp\left(\frac{15J}{2kT}\right) \end{array} \right\}}{\left\{ \begin{array}{c} 2\exp\left(\frac{-10J}{kT}\right) + 4\exp\left(\frac{-17J}{2kT}\right) + 2\exp\left(\frac{-7J}{kT}\right) + 6\exp\left(\frac{-6J}{kT}\right) + 4\exp\left(\frac{-11J}{2kT}\right) \\ + 4\exp\left(\frac{-7J}{2kT}\right) + 6\exp\left(\frac{-3J}{kT}\right) + 8\exp\left(\frac{5J}{2kT}\right) + 6\exp\left(\frac{J}{kT}\right) + 6 \\ + 8\exp\left(\frac{J}{2kT}\right) + 10\exp\left(\frac{2J}{kT}\right) + 8\exp\left(\frac{5J}{2kT}\right) + 10\exp\left(\frac{5J}{kT}\right) + 12\exp\left(\frac{15J}{2kT}\right) \end{array} \right\}}$$

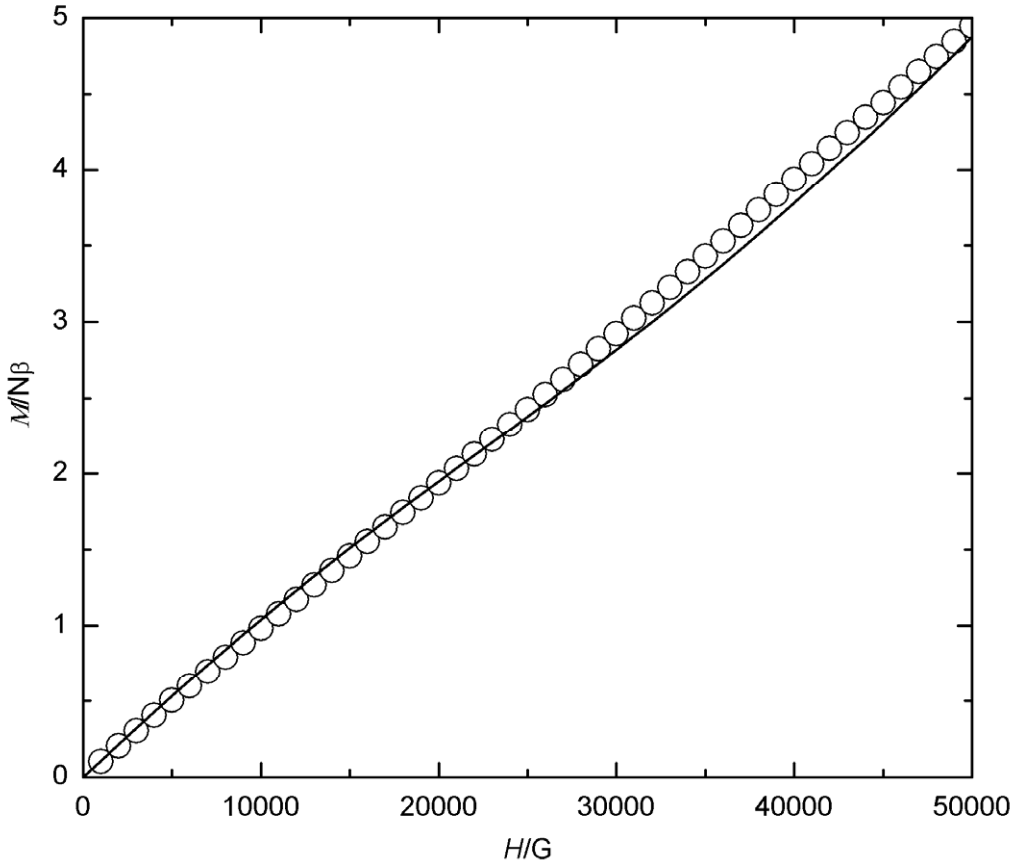

Fig S1. Field dependence of the magnetisation of **2** at 2 K (○) with the calculated curve using parameters given in main text (J = -1.80 cm^{-1}, g_{Co} = 2.29 and g_{Mn} = 2.00).