

## Supporting Information

### Materials and methods

Complex **1** was prepared according to Method 2 described by Sowrey et al.<sup>1</sup>

**Caution!** Although no such tendency was observed during the current work, perchlorate salts are potentially explosive and should be handled with care and in small quantities.

Its identity was verified by IR spectroscopy, microanalyses and powder XRD (Figure S1). Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Perkin-Elmer 2400/II automatic analyzer. Infrared spectra were recorded as KBr pellets in the range 4000-400 cm<sup>-1</sup> on a Bruker Equinox 55/S FT-IR spectrometer. Powder XRD data were collected on a D500 Siemens diffractometer equipped with a secondary graphite monochromator. Variable-temperature magnetic susceptibility measurements were carried out on powdered samples in the 2-300 K temperature range using a Quantum Design MPMS SQUID susceptometer. Diamagnetic corrections for the complexes were estimated from Pascal's constants. The magnetic susceptibility has been computed by exact calculation of the energy levels associated with the spin Hamiltonian, through diagonalization of the full matrix with a general-symmetry program.<sup>2</sup> Least-squares fittings to the dc data were accomplished with an adapted version of the function-minimization program MINUIT.<sup>3</sup>

The error-factor  $R$  is defined as  $R = \sum \frac{(\chi_{\text{exp}} - \chi_{\text{calc}})^2}{N\chi_{\text{exp}}^2}$  where  $N$  is the number of experimental

points. Ac susceptibility experiments between 111-9111 Hz were carried out on a Quantum Design PPMS magnetometer. X-band EPR measurements were obtained with an upgraded Bruker ER-200D spectrometer interfaced to a personal computer and equipped with an Oxford ESR 900 cryostat, an Anritsu MF76A frequency counter and a Bruker 035M NMR gaussmeter (EPR conditions: Temperature, 4.2K; microwave power, 50 mW; modulation amplitude, 2.5 mT; microwave frequency 9.43 GHz). Theoretical simulations of the EPR spectra were obtained with the SpinCount program kindly provided by Prof. M. P. Hendrich, Dept of Chemistry, Carnegie Mellon University, Pittsburgh, PA, U.S.A.

### Antisymmetric Exchange in trinuclear clusters.

The role of Antisymmetric Exchange (AE) in modulating the magnetic properties of antiferromagnetically coupled trinuclear transition metal clusters comprising half integer spin ions, has been discussed in references 9 and 10.<sup>4</sup> It is well known that AE does not affect the static magnetic susceptibility measurements at high temperatures ( $T > 20$  K in the present work) and the isotropic model (equation 2) is a very good approximation for modeling the data. The effects of AE are more apparent at low temperatures and this leads to  $\chi_M T$  values that are significantly smaller than those expected in the absence of it. The value of 0.26 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K in the present case is

significantly smaller than the anticipated one ( $0.36 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ). The anisotropy of the  $S = 1/2$  ground state with  $g_{\perp} \ll 2.0$  suggested by the EPR data would yield an average value of  $0.21 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ . The difference between the static magnetic susceptibility measurements and EPR spectroscopy is attributed to the presence of paramagnetic impurities such as monomeric high spin ferric species. We estimate that such a contribution would account for  $\sim 1.5\%$  of total spin centers. A closer inspection of the EPR spectra (figure S4) reveals the presence of a weak signal at  $g = 4.3$  typical for monomeric high spin ferric species.

Apart from the significant anisotropy of the  $S = 1/2$  ground state, AE critically affects the energy levels between the spin manifolds. In particular, (a) it contributes to the separation of the two  $S = 1/2$  ground states and (b) it results in zero-field splitting of the states with  $S > 1/2$ . The analysis of the IINS data in reference 7 did not take into account the role of AE. This technique maps of the energy separation between the ground state and the excited spin manifolds. However, the role of AE in the separation of the energy levels (used to extract the isotropic exchange coupling constants) was not considered. Revisiting the IINS data is beyond the scope of the present manuscript, however we estimate that omission of AE in analyzing the IINS data may result in slightly different exchange coupling constants of a few ( $< 5$ )  $\text{cm}^{-1}$ .

### Treatment of ac data

Equation (4) may be decomposed into its real and imaginary parts:<sup>5</sup>

$$\chi'(\omega) = \chi_s + \frac{\chi_T - \chi_s}{2} \left[ 1 - \frac{\sinh[(1-\alpha)\ln(\omega\tau)]}{\cosh[(1-\alpha)\ln(\omega\tau)] + \sin(\frac{1}{2}\alpha\pi)} \right] \quad (\text{S1})$$

$$\chi''(\omega) = \frac{\chi_T - \chi_s}{2} \left[ \frac{\cos(\frac{1}{2}\alpha\pi)}{\cosh[(1-\alpha)\ln(\omega\tau)] + \sin(\frac{1}{2}\alpha\pi)} \right] \quad (\text{S2})$$

Combination of S1 and S2 leads to equation S3:

$$\chi''(\chi') = -\frac{\chi_T - \chi_s}{2 \tan[\frac{1}{2}\pi(1-\alpha)]} \left[ \left( \frac{\chi_T - \chi_s}{2} \right)^2 - \left( \frac{\chi_T - \chi_s}{2 \tan[\frac{1}{2}\pi(1-\alpha)]} \right)^2 - \left( \chi' - \frac{\chi_T + \chi_s}{2} \right)^2 \right]^{\frac{1}{2}} \quad (\text{S3})$$

which is used to simulate the Cole-Cole plots.

The last equation allows the determination of  $\chi_T$ ,  $\chi_s$  and  $\alpha$ . The relaxation time  $\tau$  may be derived from Equations (1) and (2).

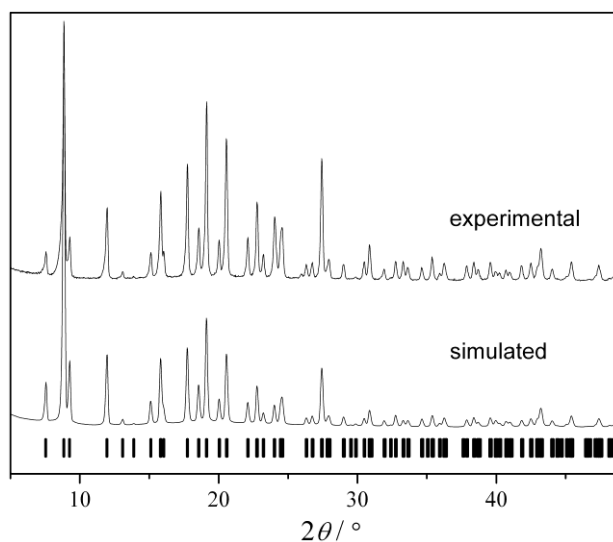


Figure S1. XRD pattern of **1** and simulation according to its crystal structure.

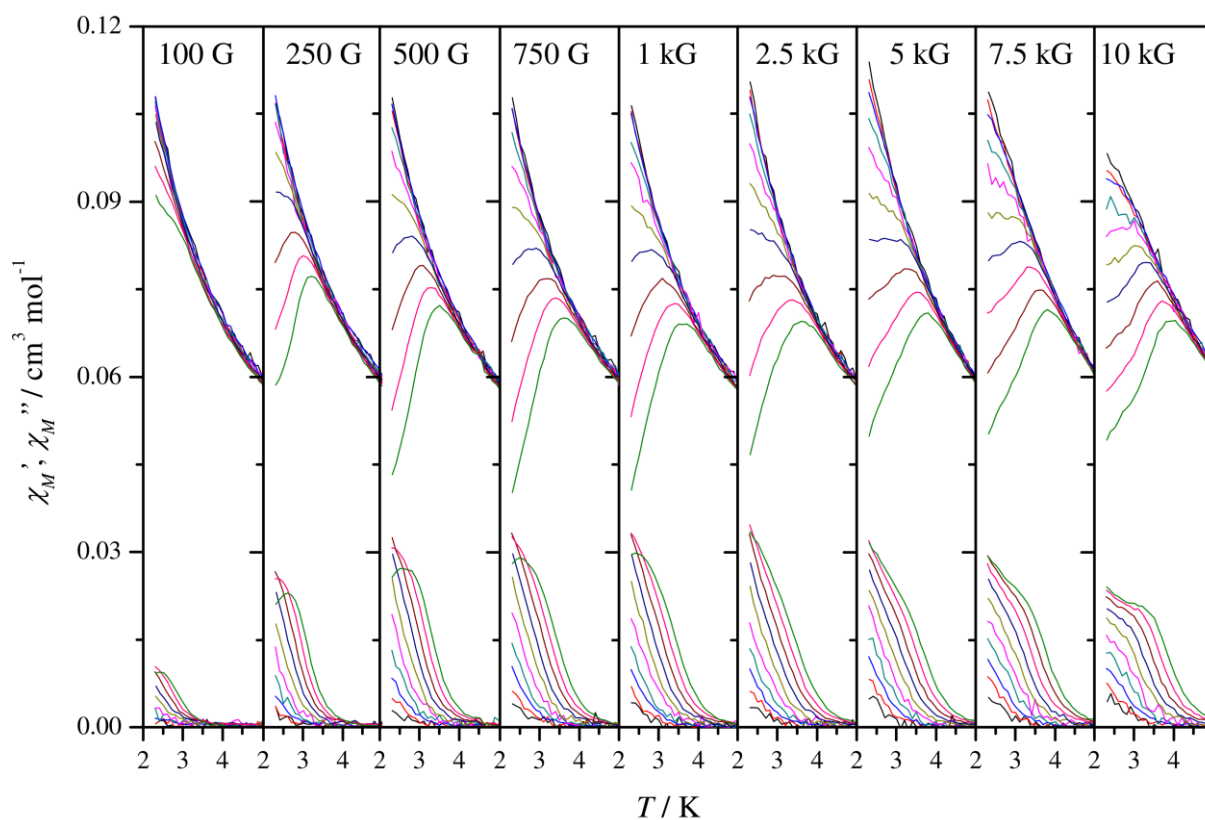


Figure S2. Variable-temperature ac susceptibility data of **1**, at various fields and frequencies.

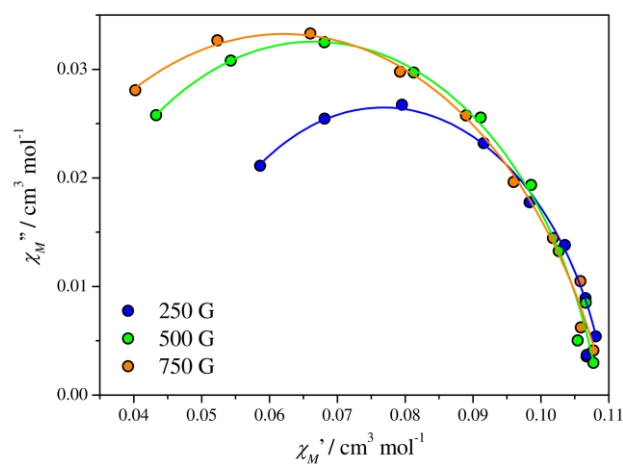


Figure S3. Cole-Cole plots at 2.3 K, under three different magnetic fields. The solid lines are fits according to Equation (S3).

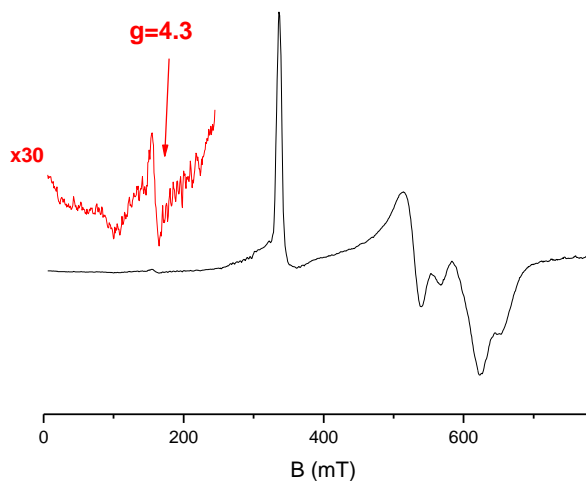


Figure S4. The EPR spectrum of figure 2 with a magnification in the low field region.

Table S1. Fits to the out-of-phase signals at various fields and temperatures.

$H$ (G)	$T$ (K)	$\chi_T - \chi_S$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$\alpha$	$\tau$ ( $10^{-5}$ s)
250	2.3	0.063(1)	0.11(1)	4.1(1)
	2.4	0.058(1)	0.06(1)	3.48(8)
	2.5	0.055(1)	0.05(2)	2.9(1)
	2.6	0.053(1)	0.07(2)	2.4(1)
	2.7	0.050(1)	0.07(1)	2.0(1)
	2.8	0.045(1)	0.02(1)	1.77(8)
	2.9	0.042(2)	0.02(2)	1.4(1)
	3.0	0.045(7)	0.08(4)	0.9(2)

	3.1	0.06(2)	0.16(4)	0.4(2)
	3.2	0.07(7)	0.20(8)	0.2(3)
500	2.3	0.082(1)	0.14(1)	4.5(1)
	2.4	0.079(1)	0.15(1)	3.8(1)
	2.5	0.076(1)	0.14(1)	3.2(1)
	2.6	0.070(1)	0.12(1)	2.8(1)
	2.7	0.0676(9)	0.126(9)	2.40(5)
	2.8	0.063(1)	0.10(1)	2.05(7)
	2.9	0.060(1)	0.10(1)	1.72(6)
	3.0	0.052(2)	0.07(2)	1.5(1)
	3.1	0.054(3)	0.10(2)	1.1(1)
	3.2	0.048(9)	0.07(5)	1.0(3)
	750	2.3	0.091(1)	0.19(1)
2.4		0.089(1)	0.20(1)	3.5(1)
2.5		0.086(1)	0.20(1)	3.0(1)
2.6		0.079(1)	0.18(1)	2.6(1)
2.7		0.074(1)	0.17(1)	2.3(1)
2.8		0.070(2)	0.16(1)	2.0(1)
2.9		0.064(10)	0.13(1)	1.81(9)
3.0		0.059(2)	0.12(1)	1.6(1)
3.1		0.056(5)	0.12(3)	1.4(2)
3.2		0.058(7)	0.15(3)	0.9(2)

Table S2. Fits to the Cole-Cole plots at various fields and temperatures.

$H$ (G)	$T$ (K)	$\chi_T$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\chi_S$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\alpha$
250	2.3	0.1115(6)	0.042(1)	0.13(1)
	2.4	0.106(1)	0.041(6)	0.12(5)
	2.5	0.101(1)	0.044(7)	0.08(7)
	2.6	0.098(1)	0.042(5)	0.08(4)
	2.7	0.0951(8)	0.043(5)	0.07(4)
	2.8	0.0928(3)	0.034(6)	0.12(1)
	2.9	0.088(2)	0.04(2)	0.03(?)
	3.0	0.088(2)	0.03(1)	0.11(8)
	3.1			

	3.2	0.0836(3)	0.035(6)	0.12(1)
500	2.3	0.111(1)	0.022(4)	0.15(2)
	2.4	0.108(1)	0.020(4)	0.16(2)
	2.5	0.104(1)	0.022(3)	0.15(1)
	2.6	0.100(1)	0.022(5)	0.15(2)
	2.7	0.095(1)	0.029(4)	0.09(3)
	2.8	0.095(1)	0.019(7)	0.16(3)
	2.9	0.0897(6)	0.031(4)	0.08(2)
	3.0	0.0878(4)	0.028(5)	0.10(1)
	3.1	0.0854(4)	0.028(4)	0.10(2)
	3.2	0.084(1)	0.0085(4)	0.014(2)
750	2.3	0.116(2)	0.009(4)	0.20(1)
	2.4	0.110(1)	0.011(4)	0.19(1)
	2.5	0.106(2)	0.013(5)	0.18(2)
	2.6	0.1050(6)	0.009(1)	0.202(6)
	2.7	0.106(2)	0.013(5)	0.18(2)
	2.8	0.097(1)	0.012(5)	0.19(1)
	2.9	0.092(1)	0.022(3)	0.14(1)
	3.0	0.0863(7)	0.033(5)	0.05(4)
	3.1	0.089(2)	0.01(1)	0.18(4)
	3.2	0.0831(2)	0.028(3)	0.10(1)

<sup>1</sup> F. E. Sowrey, C. Tilford, S. Wocadlo, C. E. Anson, A. K. Powell, S. M. Bennington, W. Moontfrooij, U. A. Jayasooriya, R. D. Cannon, *Dalton Trans*, 2001, 862-866.

<sup>2</sup> (a) J. Aussoleil, P. Cassoux, P. de Loth and J-P. Tuchagues *Inorg. Chem.*, 1989, **28**, 3051. (b) J. M. Clemente-Juan, C. Mackiewicz, M. Verelst, F. Dahan, A. Bousseksou, Y. Sanakis and J.-P. Tuchagues, *Inorg. Chem.*, 2002, **41**, 1478.

<sup>3</sup> F. James, M. Roos, "MINUIT Program, a System for Function Minimization and Analysis of the Parameters Errors and Correlations", *Comput. Phys. Commun.* **1975**, *10*, 345.

<sup>4</sup> For a recent review see also R. Boca, R. Herchel, *Coord. Chem. Rev.*, 2010, **254**, 2973-3021.

<sup>5</sup> C. Dekker, A. F. M. Arts, H. W. de Wijn, A. J. van Duynevelt, J. A. Mydosh, *Phys. Rev. B*, 1989 (*40*), 11243-11251.