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Quantum Monte Carlo Simulations and High-Field Magnetization Studies of Antiferromagnetic Interactions in a Giant Hetero-Spin Ring**

Lei Qin,¹ Jared Singleton,² Wei-Peng Chen,¹ Hiroyuki Nojiri,³ Larry Engelhardt,^{2,*} Richard E. P. Winpenny^{4,*} and Yan-Zhen Zheng^{1,*}

Abstract: We report chromium-lanthanide heterometallic wheel complexes $\{Cr_8Ln_8\}$ ($Ln = Gd, Dy$ and Y) with alternating metal centers. Quantum Monte Carlo simulations reveal antiferromagnetic exchange-coupling constants with an average of 2.1 K within the $\{Cr_8Gd_8\}$ wheel, which leads to a large ground spin state ($S_T = 16$) that is confirmed by magnetization studies up to 20 Tesla. The $\{Cr_8Dy_8\}$ wheel is a single-molecule magnet.

Understanding magnetic interactions is at the heart of molecular magnetism, a research field that leads to the exciting discovery of single-molecule magnets,^{1,2} single-chain magnets,³ molecular magnetic refrigerants,⁴ spin-based qubits⁵ and single-molecule toroids.⁶ Cyclic polymetallic compounds are of particular interest as models of infinite 1D chains, but with finite size, which may provide deeper insight to the magnetic interactions and excitations. Particularly relevant to the work reported here are mixed metal rings incorporating both 3d and 4f metal ions are less. Examples include $\{Mn^{III}_4Ln_4\}$,^{7a} $\{Mn^{III}_8Ln_8\}$,^{7b} $\{Fe^{III}_{10}Ln_{10}\}$,⁸ $\{Ni^{II}_{12}Ln_{36}\}$,^{9a} $\{Cu^{II}_{36}Ln_{24}\}$ ^{9b} and $\{Co^{II}_{16}Ln_{24}\}$.^{9c} Cr(III)-based heterometallic 3d-4f rings include $\{Cr^{III}_3Ln_3\}$ and $\{Cr^{III}_4Ln_4\}$ reported by the Powell group,¹⁰ and $\{Cr^{III}_6Ln_2\}$ and $\{Cr^{III}_{12}Ln_4\}$ cages reported by McRobbie *et al.*¹¹

Here we report the largest Cr(III)-Ln(III) heterometallic wheel, $[Cr_8Ln_8(mdea)_{16}(CH_3COO)_8(NO_3)_8] \cdot xCH_3CN$ (**1**) ($mdeaH_2 = N$ -methyldiethanolamine, $x = 3, 6$ and 3 for **1-Gd**, **1-Dy** and **1-Y**, respectively) with sixteen alternating Cr and Ln metal centers. High-Field Magnetization and quantum Monte Carlo (QMC) simulation¹²⁻¹⁴ studies indicate that **1-Gd** displays a ferrimagnetic ground state ($S_T = 16$) due to the antiferromagnetically-coupled

neighbouring spins. The **1-Dy** complex shows slow magnetic relaxation and *non-tunneling* zero-field magnetic hysteresis loop at low temperatures, and together with the absence of frequency-dependent ac susceptibility of a diluted sample, suggests an unusual molecule-originated magnet-type behaviour in large 3d-4f mixed metal clusters.

All of the three complexes are isostructural and crystallize in the orthorhombic space group Fdd (Figure 1 and Table S1). Hence, the structure of **1-Gd** is described as representative. In **1-Gd**, the eight Cr(III) and eight Gd(III) ions are arranged alternately to form a ring with C_2 symmetry. Each Cr(III) atom is six-coordinate, bound to O-donors provided by three 3.212 (in Harris notation¹⁵) $mdea^{2-}$ ligand (Figure S1) and one 2.11 acetate ligand; the acetate is generated in situ from acetylacetone or acetonitrile under solvothermal conditions.¹⁶ For each Gd(III) site, the coordination is similar to Cr(III) sites except for an additional 1.11 nitrate anion, affording the eight-coordinate environment. The Cr–O distances are from 1.96 to 2.00 Å while the Gd–O distances are from 2.32 to 2.52 Å (Table S2). The Cr–N and Gd–N distances are in the range from 2.14 to 2.15 Å and from 2.65 to 2.94 Å, respectively. The Cr...Gd distances alternate between 3.48 Å and 3.37 Å. In the single crystal the molecules pack in an ABAB fashion (Figure S2).

Figure 1. a) The molecular structure of complex **1-Gd**. Color codes: Cr, aqua; Gd, violet; C, gray; N, blue; O, little orange. The hydrogen atoms were omitted for clarity.

Dc magnetic susceptibilities of poly-crystalline samples of **1-Gd** and **1-Dy** and **1-Y** were measured from 0.5 to 300 K (for **1-Y** data were measured 2.0 to 300, see supporting information) (Figure 2a and S3). At room temperature, the χT products (in unit of $cm^3 mol^{-1} K$) of three samples are all in good agreement with the expected values for eight non-interacting Cr(III) and

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eight non-interacting Ln(III) ions. Upon cooling, **1-Gd** and **1-Dy** show similar behaviors where the χT product decreases slowly down to a minimum at ca. 6 K before abruptly increasing. For **1-Y**, the χT product is roughly constant until 10 K, followed by a slow increase to 2 K. For **1-Gd**, **1-Dy** and **1-Y**, the Curie-Weiss fitting for the χ^{-1} vs. T plots affords Curie constants (C) of 78.9, 132.8 and 14.8 cm³ mol⁻¹ K and Weiss constant (θ) of -8.53, -13.41 and 2.19 K (Figure S4), respectively. These behaviors indicate dominant antiferromagnetic interactions in **1-Gd** and **1-Dy** and weak ferromagnetic interaction in **1-Y**.

Figure 2. (a) Temperature-dependent dc magnetic susceptibility plots (dots) and QMC calculations (lines, see text below) for **1-Gd** under the field of 1000 (blue) and 5000 Oe (green). Insert: amplifying the $T < 5$ K data. (b) Field-dependent magnetization data (dots) and QMC calculations (lines) from 0.5 to 1.5 K (color codes: 0.5 K, blue; 1.0 K, cyan; 1.5 K, yellow) for **1-Gd**. Insert: the magnetization data at 0.5 K together with the Brillouin function plot (red line) of $S = 16$ for $g = 2.0$ and the proposed spin arrangement diagram for the ground state.

For **1-Gd**, $M(H)$ measurements show that magnetisation saturates before 1 T and remains constant to 5 T before increasing again (0.5–1.5 K, Figure 2b). The magnetization saturates more slowly at higher temperatures (Figure S5). At 0.5 K, the magnetization values of the flat region are all around 32–34 μ_B which suggest an $S = 16$ ground state. In addition, the Brillouin function for $S = 16$ ($g = 2.0$) at 0.5 K agrees well with the experimental data, especially when the field is lower than 4 T (insert in Figure 2b), suggesting a well isolated ferrimagnetic spin ground state. The non-zero slope of M vs. H at higher fields should be originated from the partial population of the low-lying

excited states, which is consistent with the trend seen here that this slope decreases as the temperature is lowered from 1.5 to 0.5 K. A possible schematic diagram for the spin arrangements (insert in Figure 2b) was proposed for the ferrimagnetic state.

For **1-Dy**, the field-dependent magnetization was also measured from 0.5 K to 4 K (Figure S6). The magnetizations at 0.5 K and 7 T are 52.5 μ_B without saturations. This indicates the presence of significant magnetic anisotropy and/or the population of low-lying excited states in this complex. For **1-Y**, the magnetization plots from 2 K to 4 K were measured (Figure S7), the value at 2 K and 7 T is 24.0 μ_B , in accordance with the saturation value for eight Cr(III) ions. The plot at 2 K is a similar to the Brillouin function for eight non-interacting Cr(III) ions but M increases slightly more rapidly which confirms the weak ferromagnetic interaction between the Cr(III) ions.

Although the wheel-like geometry provides a relatively simple magnetic interaction pathway, the Hilbert space for **1-Gd** is still too large to perform matrix diagonalization ($\sim 10^{12}$). Herein, we simulated the magnetic data using a quantum Monte Carlo method with the stochastic series expansion implementation from Algorithms and Libraries for Physics Simulations (ALPS) for **1-Gd** (Figures 2 and 3).^{12–14} Because the Cr...Gd distances are not all equal and can be divided into two subgroups (3.37 and 3.48 Å), a two- J model based on the following Hamiltonian was used:

$$\hat{H} = J_1 \sum_{i=1}^8 \hat{S}_{Cr_i} \cdot \hat{S}_{Gd_i} + J_2 \sum_{i=1}^7 \hat{S}_{Cr_{i+1}} \cdot \hat{S}_{Gd_i} + J_2 \sum_{i=1}^8 \hat{S}_{Cr_i} \cdot \hat{S}_{Gd_8} - \mu_B H \sum_{i=1}^8 g_{Cr} \hat{S}_{Cr_{iz}} - \mu_B H \sum_{i=1}^8 g_{Gd} \hat{S}_{Gd_{iz}} + \sum_{i=1}^8 D_{Cr} \hat{S}_{Cr_{iz}}^2$$

This model uses the sign convention where $J > 0$ represents an antiferromagnetic interaction, but also included a single zero-field splitting term, D_{Cr} , for each Cr(III) site. The symbol $\hat{S}_i$ denotes the spin vector operator for site i and g is the Landé factor. All J values will be reported in units of Kelvin (K), meaning that J/k_B has the value reported, given in units of K. The system consists of eight Cr(III) ions and eight Gd(III) ions, where each Cr(III) ion has $s = 3/2$, and each Gd(III) ion has $s = 7/2$. Hence, the two- J alternate around the ring as (J_1, J_2, J_1, J_2 , etc., Figure S8). The plots in Figure 2 show experiment and theory for the two- J model, using the parameters which gave the best fit: $J_1 = 0.74$ K, $J_2 = 3.46$ K, $D_{Cr} = 0.175$ K, $g_{Cr} = 1.98$ and $g_{Gd} = 2.03$. The J values determined the shape of the curves for $T > 2$ K, and the curvature of the plot for $T < 2$ K is determined by the value of D_{Cr} . The effect of the J_2/J_1 ratio on the theoretical data was also shown in Figure S9, where the susceptibility plots were displayed using different J_2/J_1 ratios with a fixed value of the average, $(J_1 + J_2)/2 = 2.1$ K. A ratio of $J_2/J_1 = 1$, which corresponds to the single- J model, does not provided a deep enough “dip” to match the experimental data around $T = 5$ to 10 K. As the ratio J_2/J_1 is increased, this dip becomes deeper, and a ratio of $J_2/J_1 > 4$ is needed in order to fit the data in this temperature range.

To confirm this Monte Carlo calculation, we measured the high-field magnetization using a pulsed magnetic field up to about 20 T (a full cycle from 0 to 20 T and then go back to 0 T)

at 0.4 K (Figure 3). When the field is larger than 7 T, the magnetization continues to increase until to the saturation value around 18–20 T. The near linear increase from 7 to 16 T shows the dominant antiferromagnetic interactions in **1-Gd** system. There is some small hysteresis that can be seen in the experimental data between the up and down cycle, particularly in the range $0 < H < 2$ T which originates from the competition between the thermal relaxation and the fast change of the magnetic field.¹⁷ In this range, the upper curve matches the theory data very well. There are some deviations that are probably due to some anisotropy in the system. For example, the theory predicts small “wiggles” in M vs. H between 8 and 16 T where the experimental data are smooth. The wiggles in the theory data are due to ground-state level crossings, which could be smoothed out in the experimental data if these level crossings are replaced by avoided crossings, caused by the slight anisotropy.

Figure 3. Field-dependent magnetization data (black lines) and QMC calculation (red dots) at 0.4 K for **1-Gd**.

Alternating-current (ac) susceptibility measurements were also carried out on these three samples. For **1-Gd** and **1-Y**, no slow magnetic relaxation behaviors were observed (Figure S10). Compound **1-Dy** shows in-phase (χ') and out-of-phase (χ'') signals that are temperature- and frequency-dependent under zero dc field (Figures S11 and S12). The Cole–Cole plots of χ' versus χ'' from 1.9 to 2.7 K suggest a single relaxation process is operational, which can be fitted using a generalized Debye model with α values ranging from 0.04 to 0.13. Evaluated from the relaxation time τ (Table S3), the linear plot of $\ln(\tau)$ versus $1/T$ was revealed, implying an Orbach process is dominant over the measured temperature and frequency span. The fitting of the Arrhenius law $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$ affords the U_{eff} of 19.0 K with $\tau_0 = 3.5 \times 10^{-8}$ s, which is reasonable compared to other SMMs.²

We measured the magnetic hysteresis plots of **1-Dy** which shows an open magnetic hysteresis loop at 0.5 K (Figure 4). The coercive field of the open hysteresis is about 1400 Oe with average sweep field rate of 6 Oe s⁻¹. This we ascribe to the Cr(III)–Dy(III) interactions which effectively suppress the zero-field QTMs. This phenomenon was also observed in some other Cr(III)–Dy(III) systems.¹⁸ Further ac susceptibility measurements

were made on a sample of single Dy^{III} ions doped into **1-Y**, namely **1-Y_{0.954}Dy_{0.046}** (see supporting information and Table S4); these show no slow relaxation of magnetisation (Figure S13). Therefore, we can conclude that the slow magnetic relaxation behavior of **1-Dy** is originated from the molecule based on Cr(III)–Dy(III) exchange-couplings rather than the single ion origin of Dy(III) ions.

Figure 4. Magnetic hysteresis plots at 0.5 and 1.0 K for **1-Dy** with average sweep field of 6 Oe s⁻¹.

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Keywords: cyclic coordination clusters • Cr–Ln • Quantum Monte Carlo • exchange-coupling • single-molecule magnets

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COMMUNICATION

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Quantum Monte Carlo
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The exchange-coupling constants of the largest Cr(III)-Ln(III) wheel was exactly predicted and experimentally confirmed using pulsed high field magnetization technique, which leads to a large ground spin state ($S_T = 16$) for the Gd analogue and a tunnelling-free single-molecule magnet behavior for the Dy analogue.