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Hymas, Kieran , Soncini, Alessandro , Vignesh, Kuduva R , Chauhan, Deepanshu, Swain, Abinash, Benjamin, Sophie L , Borah, Dipanti, Shanmugam, Maheswaran, Wernsdorfer, Wolfgang , Rajaraman, Gopalan, Langley, Stuart K and Murray, Keith S (2024) Discriminating ferrotoroidic from antiferrotoroidic ground states using a 3d quantum spin sensor. npj Quantum Materials, 9 (1). 106 ISSN 2397-4648

# DOI: https://doi.org/10.1038/s41535-024-00712-9

Publisher: Springer

Version: Supplemental Material

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**Data Access Statement:** The X-ray crystallographic coordinates for the structure reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number 2106845. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. The Mathematica notebooks used for the implementation of the theoretical models of spin dynamics and electron paramagnetic resonance are available from the corresponding authors upon reasonable request.

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# Supplementary Information: Discriminating ferrotoroidic from antiferrotoroidic ground states using a 3d quantum spin sensor

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(Dated: October 30, 2024)

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#### I. CRYSTAL DATA AND STRUCTURE REFINEMENT FOR ${\rm Cr}{\rm D}y_3$

Supplementary Table 1: Crystal data and structure refinement. <sup>a</sup> Including solvate molecules. <sup>b</sup> Graphite monochromator. <sup>c</sup>  $R_1 = \sum ||F_O| - |F_C|| / \sum |F_O|, wR_2 = \left(\sum \left[w(F_O^2 - F_C^2)^2\right] / \sum \left[w(F_O^2)^2\right]\right)^{1/2}$ .

	1
Formula <sup>a</sup>	$Dy_3CrC_{36}H_{50}O_{27}$
$M/[\text{g mol}^{-1}]$	1609.03
Crystal system	Orthorhombic
Space group	Pnma
$a/[ m \AA]$	19.4471(4)
$b/[ m \AA]$	21.1752(4)
$c/[{ m \AA}]$	17.3815(6)
$\alpha/[^{\circ}]$	90
$\beta/[^{\circ}]$	90
$\gamma/[^{\circ}]$	90
$V/[A^{-1}]$	7157.6(2)
T/K	123(2)
Z	4
$ ho_{ m calc} \; [{ m g} \; { m cm}^{-3}]$	1.471
$\Lambda^{ m b}$ /[Å]	0.71073
Data Measured	34446
Ind. Refins	8982
$R_{ m int}$	0.0414
Refine with $I > 2\sigma(I)$	7003
Parameters	391
Restraints	35
$R_1^{\rm c}$ (obs), wR <sub>2</sub> <sup>c</sup> (all)	0.0645,  0.1729
Goodness of fit	1.119
Largest residuals/[ $e \ \text{\AA}^{-3}$ ]	4.711, -1.523

KDs	Dy1	Dy2	Dy3
1	0.0	0.0	0.0
2	152.6	140.1	129.2
3	225.8	216.4	202.8
4	264.8	246.2	224.3
5	320.4	281.3	247.1
6	345.7	306.2	286.5
7	386.5	352.3	338.7
8	431.5	427.5	425.1

Supplementary Table 2: RASSI energies  $(cm^{-1})$  of the 8 lowest-lying Kramer's doublets (KDs) for isolated Dy<sup>III</sup> ions in compound **1**.



Supplementary Figure 1: CASSCF computed ground to first excited state energy gaps in  $Dy^{III}$  ions of  $CrDy_3$  as function of  $H_2O$  orientation. Black data points depict results of calculations conducted on the  $CrDy_3$  crystal structure. The blue and red data points are results from the same calculations however with the H-O bonds of each water molecule oriented parallel and perpendicular (respectively) to the plane of the isonicotinate ligand which coordinates with the relevant  $Dy^{III}$  and  $Cr^{III}$  ions.

KDs	g	Dy1	Dy2	Dy3
	$g_x$	0.012	0.014	0.045
1	$g_y$	0.025	0.021	0.059
	$g_z$	19.560	19.470	19.379
	$g_x$	0.698	0.603	1.199
2	$g_y$	1.090	0.691	1.549
	$g_z$	15.524	15.668	15.143
	$g_x$	3.784	2.820	1.050
3	$g_y$	4.629	4.095	2.791
	$g_z$	11.558	11.542	10.761
	$g_x$	0.376	9.646	1.119
4	$g_y$	4.851	6.030	5.435
	$g_z$	9.393	0.999	13.347
	$g_x$	0.359	2.118	1.91
5	$g_y$	5.187	4.439	5.824
	$g_z$	10.148	13.528	13.104
	$g_x$	1.430	0.114	0.287
6	$g_y$	4.351	0.572	0879
	$g_z$	15.508	17.156	18.014
	$g_x$	0.143	0.309	0.286
7	$g_y$	0.615	0.586	0.483
	$g_z$	18.874	18.546	18.764
	$g_x$	0.119	0.080	0.030
8	$g_y$	0.291	0.095	0.058
	$g_z$	19.288	19.478	19.586

**Supplementary Table 4:** RASSI energies (cm<sup>-1</sup>) of the 8 lowest-lying Kramer's doublets (KDs) for isolated Dy<sup>III</sup> ions in compound **1** with water molecules rotated parallel to isonicotinate ligands.

KDs	Dy1	Dy2	Dy3
1	0.0	0.0	0.0
2	143.2	82.3	113.3
3	218.7	121.9	155.0
4	256.9	180.514	209.1
5	310.1	213.9	256.3
6	358.8	247.3	291.7
7	377.0	159.8	376.0
8	392.4	369.7	412.0

KDs	Dy1	Dy2	Dy3
1	0.0	0.0	0.0
2	146.7	149.4	132.6
3	240.7	262.1	221.6
4	285.1	327.1	274.7
5	328.3	364.9	302.3
6	393.8	396.9	343.2
7	420.6	484.3	364.2
8	492.0	534.7	500.7

Supplementary Table 5: RASSI energies  $(cm^{-1})$  of the 8 lowest-lying Kramer's doublets (KDs) for isolated Dy<sup>III</sup> ions in compound 1 with water molecules rotated perpendicular to isonicotinate ligands.

Supplementary Table 6: RASSI energies  $(cm^{-1})$  of the 8 lowest-lying Kramer's doublets (KDs) for isolated Dy<sup>III</sup> ions in compound 1 with water molecules rotated 45° to isonicotinate ligands.

KDs	Dy1	Dy2	Dy3
1	0.0	0.0	0.0
2	132.1	129.1	112.9
3	191.1	162.9	167.0
4	230.4	231.2	192.6
5	276.0	295.7	221.0
6	330.9	330.6	262.8
7	379.8	345.6	345.7
8	444.4	389.4	365.8

Supplementary Table 7: RASSI energies (cm<sup>-1</sup>) of the 8 lowest-lying Kramer's doublets (KDs) for isolated Dy<sup>III</sup> ions in compound 1 with water molecules rotated 135° to isonicotinate ligands.

KDs	Dy1	Dy2	Dy3
1	0.0	0.0	0.0
2	132.3	129.4	127.5
3	207.4	173.2	198.2
4	239.5	218.5	235.5
5	285.7	273.5	253.3
6	339.3	326.7	313.8
7	376.3	343.7	355.7
8	436.8	362.2	432.6



Supplementary Figure 2: (top) Time evolution of the  $CrDy_3$  spin state populations on forward trace of the applied magnetic field at a rate of  $\omega = 0.28 \text{ T s}^{-1}$ . The colour coding of the populations matches that of the Zeeman diagram in the main text with the blue and yellow curves depicting the time evolution of the first and second excited  $Cr^{III}$  spin states, respectively, with a clockwise (dark) and anticlockwise (light)  $Dy_3$  toroidal configuration. The grey solid lines depict the time-evolution of the  $Dy_3$  magnetic configuration populations. The time-evolution of the four adiabatically evolving  $Cr^{3+}$  spin states (with toroidal  $Dy_3$  configurations) are also shown to illustrate the quantum superposition of the  $Cr^{III}$  spin states owing to competing magnetic interactions. (bottom) Magnetic hysteresis simulation against experiment from the main text for reference.

#### IV. SUPPLEMENTARY NOTE 1: ALTERNATIVE EXPLANATION FOR THE CrDy<sub>3</sub> SICKLE-SHAPED MAGNETISATION

In this section, we propose an alternative explanation for the sickle-shaped single-crystal magnetisation for  $\text{CrDy}_3$ which entails a magnetic response originating solely from the  $\text{Cr}^{3+}$  ion, weakly coupled to the toroidal ground state of the Dy<sub>3</sub> triangular lanthanide moiety. Using the same theoretical model from the main text, with the anisotropy axes of all paramagnetic species fixed by the *ab initio* results, we simulated the experimental single-crystal magnetisation curve (Figure 2 of the main text) by allowing the exchange coupling parameters  $J_1$  and  $J_2$ , and the magnetic field orientation  $\eta_F$  and  $\phi_F$  to vary.

Given the small hysteresis loops of magnetization observed in the experimental curves, we assume that the tracing field evolves quasi-statically with respect to the fast fluctuating  $Cr^{III}$ . Hence, at each field value the sum of the molecular Hamiltonian  $H_{mol}$ , and Zeeman Hamiltonian  $H_{Zee}$ , can be diagonalised for each semi-classical Dy<sup>III</sup> spin configuration **m** of CrDy<sub>3</sub>, to yield the 32 instantaneous eigenstates  $|\mathbf{m}, \varphi_i\rangle = \sum_{M_{Cr}} C^i_{\mathbf{m}, M_{Cr}} |\mathbf{m}\rangle \otimes |M_{Cr}\rangle$  (i = 1, ..., 4) with energies  $E_{|\mathbf{m}, \varphi_i\rangle}$ . As in the main text, the field dependence of the energies  $E_{|\mathbf{m}, \varphi_i\rangle}$  and amplitudes  $C^i_{\mathbf{m}, M_{Cr}}$  is implied and we choose a quantisation axis for Cr<sup>III</sup> along the axis of the applied field. Thus, with our effective model, we simulate the single-crystal magnetisation of CrDy<sub>3</sub> and find excellent agreement with the experimental data using the values  $J_1 = 0.2 \text{ cm}^{-1}$ ,  $J_2 = -0.6 \text{ cm}^{-1}$ ,  $\eta_F = 40^\circ$  and  $\phi_F = 50^\circ$  (see Figure ??a).

The Zeeman spectrum of  $CrDy_3$  plotted in Figure ??b reveals that no level crossings occur between the toroidal ground state configurations and single or double-flipped  $Dy^{III}$  magnetic states (shown in grey) indicating that the



Supplementary Figure 3: Theoretical simulation and interpretation of single-crystal  $\mu$ -SQUID experiments. **a** Normalised simulated single-crystal magnetisation curve (orange) against  $\mu$ -SQUID single-crystal measurements (blue) at T = 0.03 K and with a field oriented  $\eta_F = 40^{\circ}$  out-of-plane with azimuthal angle  $\phi_F = 50^{\circ}$ . **b** Zeeman spectrum of the 32 dimensional Hilbert space of the effective CrDy<sub>3</sub> model. The toroidal manifolds are shown in colour whereas the single spin-flipped dysprosium magnetic states have been greyed out for clarity. The inset shows a close-up of the Zeeman spectrum of the 8 dimensional toroidal manifold for positive fields. **c** Schematic representation of the applied magnetic field (purple arrow) torquing the Cr<sup>III</sup> quantum spin sensor after aligning to the remnant magnetic moment (orange arrow) of the Dy<sub>3</sub> triangle,  $M_{\rm rem}$ , along its principal magnetic easy axis (dashed line). **d** Squared amplitudes of the  $|-\tau, \phi_1\rangle$  Cr<sup>III</sup> wavefunction against applied field.



Supplementary Figure 4: Simulated single-crystal magnetisation for  $\text{CrDy}_3$  at T = 0.03 K using the effective theoretical model presented above. Keeping all parameters from the main text fixed, we vary the out-of-plane angle  $\eta_F$  of the magnetic field.

single-crystal magnetisation is dominated by the magnetic response of the  $Cr^{III}$  ion. Nevertheless, the experimental and simulated single-crystal magnetisation differs markedly from a typical Brillouin curve expected for an isolated, free-fluctuating  $Cr^{III}$  spin.

A schematic illustration of the magnetic response of the Cr<sup>III</sup> quantum spin to the external field is shown in Figure ??c. In the absence of a magnetic field, the Cr<sup>III</sup> spin aligns along it's easy axis, roughly perpendicular to the triangular plane. By virtue of the ferromagnetic exchange coupling  $J_1$ , the spin is preferentially aligned with the remnant magnetic moment of the Dy<sub>3</sub> triangle,  $M_{\rm rem}$ , which is almost collinear with the Cr<sup>III</sup> principal anisotropy axis. The application of a small positive field exerts a magnetic torque on the Cr<sup>III</sup> spin leading to a quantum superposition of  $|M_{\rm Cr}\rangle$  spin states and hence to a slow rise in the squared amplitude of the ground state  $|M_{\rm Cr}\rangle = -3/2$  projection along the axis of the field (see purple curve in Figure ??d). Without any source of magnetic anisotropy, i.e. for a free-fluctuating spin, this alignment would be instantaneous and result in a typical Brillouin magnetisation curve. The sickle-shaped magnetisation in CrDy<sub>3</sub> at positive fields, is reflected in the square of  $C_{-\tau,-3/2}^1$  and for negative fields in the square of the time-reversed  $C_{\tau,3/2}^1$  amplitudes. Naturally, the detection of toroidal states in the single-crystal magnetisation of CrDy<sub>3</sub> depends upon dominant thermal population of the ground state (blue curve in Figure ??b) of the ground toroidal manifold. Since the splitting of these states is roughly 0.5 cm<sup>-1</sup>, toroidal moment sensing here is possible up to ~ 1 K.

In Figure ?? we show the angle dependence of this signal as a result of varying the canting of the external magnetic field  $\eta_F$ . When the field is aligned approximately along the anisotropy axis of  $\operatorname{Cr}^{3+}$  and the remnant magnetic moment of the Dy<sub>3</sub> triangle, an approximate Brouillon function is recovered. Deviating from this preferential axis however, introduces a competition between the applied field and the intrinsic magnetic anisotropy axes of the molecule, for the alignment of the  $\operatorname{Cr}^{3+}$  magnetic moment resulting in the sickle-shaped magnetisation response. In Figure ?? we deconstruct the effects of zero-field splitting of the ground  $\operatorname{Cr}^{\mathrm{III}}$  quartet and magnetic coupling to the remnant magnetisation in Dy<sub>3</sub> on the single-crystal magnetisation of  $\operatorname{CrDy}_3$ . When both interactions are absent, a Brillouin curve typical of a free-fluctuating spin  $\frac{3}{2}$  is recovered (Figure ??a) which is far from the experimentally observed sickle-shaped magnetisation. It is evident from panels b and c, that neither the inclusion of zero-field splitting nor magnetic coupling to  $M_{\text{rem}}$  alone recovers the experimental curve but rather a combination of the two (Figure ??d).

Despite the striking agreement between our model and the experimental single-crystal magnetisation results, we exclude this explanation for the sickle-shaped single-crystal magnetisation on the basis that the large value of  $J_2$ , the Dy-Dy intramolecular exchange coupling, required to isolate the Cr<sup>3+</sup> spin dynamics from Dy<sup>3+</sup>, introduces a



Supplementary Figure 5: Decomposition of interactions leading to  $\text{CrDy}_3$  magnetic response. Single-crystal magnetisation computed with our model (orange curves) superimposed to experimental data (blue curves) using parameters specified in the main text however now with **a** no zero-field splitting of  $\text{Cr}^{\text{III}}$  and no coupling to  $M_{\text{rem}}$ , **b** coupling to  $M_{\text{rem}}$  only, **c** *ab initio* determined zero-field splitting only and **d** all interactions included.

characteristic sigmoidal shape to the isothermal powder magnetisation (See Figure ??) which we do not observe in experiment. This mechanism is worth mentioning, nevertheless, as a potential alternative explanation for sickle-shaped magnetisation curves in other mixed 3d-4f SMT systems with large intramolecular lanthanide exchange.



Supplementary Figure 6: (left) Simulated powder magnetisation for  $\operatorname{CrDy}_3$  at T = 2 K using parameters described above. To simulate the random orientation of molecules in the powder we integrate the magnetisation over a Lebedev sphere with 146 points. (right) Simulated magnetic susceptibility versus temperature for  $\operatorname{CrDy}_3$  using parameters from above. Here we utilise the theoretical model in the main text however, to arrive at the correct high temperature limit associated with thermal population of all Kramers doublets of the  $\operatorname{Dy}^{\operatorname{III}}$  ions, we add in the *ab initio* computed susceptibilities and subtract away the contribution  $(\chi T)_0$  from the ground Kramers doublets of  $\operatorname{Dy}^{\operatorname{III}}$  and the ground quartet of  $\operatorname{Cr}^{\operatorname{III}}$  to avoid double counting, i.e.  $\chi T = (\chi T)_{\text{model}} + (\chi T)_{\text{ab initio}} - (\chi T)_0$ .

#### V. ANGLE-DEPENDENT $\mu$ -SQUID SIMULATIONS FOR SENSING FERROTOROIDIC OR ANTIFERROTOROIDIC GROUND STATES IN CuDy<sub>6</sub>



Supplementary Figure 7: Simulated single-crystal magnetisation for  $\operatorname{CuDy}_6$  with a ferrotoroidic (black) and antiferrotoroidic (red) ground state at T = 0.01 K using the effective theoretical model presented in the main text. Keeping all parameters from the main text fixed and restricting the field sweeping domain to  $-100 \text{ mT} \leq B \leq 100$ mT, we vary the out-of-plane angle  $\eta_F$  of the magnetic field for each figure. Note that for a ferrotoroidic ground state (black curve), the single-crystal magnetisation is unchanging with  $\eta_F$ , a response typical of an isotropic spin  $S = \frac{1}{2}$ . When the antiferrotoroidic Dy<sub>3</sub>-Dy<sub>3</sub> configuration is the ground state, the single crystal magnetisation (red curve) is sensitive to the field orientation  $\eta_F$ .

# VI. FURTHER INFORMATION ON ELECTRON PARAMAGNETIC RESONANCE SIMULATIONS FOR $CuDy_6$



Supplementary Figure 8: Zeeman diagrams for three cases of  $\operatorname{CuDy}_6$  ground state with field oriented in  $\theta_F$  from the molecular z axis (i.e. the direction of out-of-plane canting of Dy magnetic axes). Black arrows indicate possible transitions proportional to  $\nu = 6$  GHz radiation. Case 1 is achieved with  $J_1 = -0.08 \text{ cm}^{-1}$ ,  $J_2 = -0.043 \text{ cm}^{-1}$ ,  $\eta = 6.63^\circ$  and  $\phi = 0.63^\circ$ . Case 2 is achieved with  $J_1 = -0.08 \text{ cm}^{-1}$ ,  $J_2 = -0.043 \text{ cm}^{-1}$ ,  $\eta = 15^\circ$  and  $\phi = 0.63^\circ$ . Case 3 is achieved with  $J_1 = -1 \text{ cm}^{-1}$ ,  $J_2 = -0.043 \text{ cm}^{-1}$ ,  $\eta = 6.63^\circ$  and  $\phi = 0.63^\circ$ . For case 1, a resonant gap between the Cu spin states with ferrotoroidic Dy configurations (red) occurs at  $B \sim 35$  mT and does not change with field orientation. In case 2, resonant gaps occur around  $B \sim 25 - 50$  mT as well as  $B \sim 70$  mT between Cu spin states and one of the antiferrotoroidic Dy configurations (yellow); the position of these resonances is highly sensitive to field orientation leading to broadening of the EPR spectrum. In case 3, no signal is observed since the only resonant transitions are between states from different antiferromagnetic manifolds i.e. would require 6 simultaneous Dy magnetic moment flips.



Supplementary Figure 9: Simulated powder EPR spectra for three cases of  $\text{CuDy}_6$  ground state. The top row illustrate the zero temperature frequency dependence of the spectra in each of the three different cases and the bottom row shows the temperature dependence (for  $\nu = 6 \text{ GHz}$ ) of each ground state case. Spectra are offset for clarity. Both frequency and temperature dependence of case 1 is typical of an isotropic S = 1/2 spin. A series of convoluted peaks occur in case 2 as a result of the anisotropy induced by coupling of the Cu spin to the remnant magnetisation of the ground antiferrotoroidic configuration, as temperature is increased the signal flattens out. For case three, a characteristic blank spectra is observed apart from the emergence of hot transitions between T = 0.1 - 0.5 K resulting from spin transitions in the excited ferrotoroidic manifold.