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Ferromagnetic coupling in a chloride-bridged erbium single-molecule magnet†

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We present the first ferromagnetically-coupled Er^{3+} complex with linked, high-anisotropy Er–COT (COT^{2-} = cyclooctatetraene dianion) subunits. The dinuclear complex, $[Er(\mu_2\text{-}Cl)(COT)(THF)]_2$, demonstrates single-molecule magnetism with a single, zero-field magnetization relaxation barrier of U_{eff} = 113 cm^{-1}. This system offers evidence that anisotropy can be preserved in the presence of ferromagnetic linking of the Er–COT subunits, providing a rational means to build strong molecular magnets of tunable dimensionality.

Recent advances in reading and writing information to atomic and molecular-level magnetic materials have demonstrated that single-molecule magnetism (SMM) is not purely of academic interest but will inform technological applications.[1] While manipulating atomic-level spin represents a major advance, researchers are still faced with the challenge of constructing molecular magnets that can retain magnetization for longer times at higher temperatures.

Although multinuclear transition metal clusters led SMM research for many years,[2,3] much recent work has shifted towards single-ion f-block[4] and transition metal complexes.[5] With judicious choice of metal type and ligand environment, high magnetic anisotropy can be achieved. Expanding these isolated anisotropic units into molecular-cluster magnets is difficult in lanthanide systems[6] but, in a few cases, the goal has been achieved through the synthesis of lanthanide-oxo clusters,[7] lanthanide-radical bridges,[8] and lanthanide-transition metal clusters.[9] One significant issue in multinuclear systems has been that, while many lanthanides show obvious means to create highly anisotropic single-ion crystal field environments,[10] there is no readily available model for how to retain this anisotropy while transitioning to larger, exchange-coupled clusters.[11] This problem has prompted researchers to focus their attention toward the synthesis and characterization of dinuclear $\{Ln_2\}$ complexes as simple frameworks for simultaneously understanding and optimizing both anisotropy and coupling.[12]

To develop systems that evince cooperative spin effects while retaining strong single-ion anisotropy, Er^{3+} shows particular promise because even a single cyclooctatetraene dianion (COT^{2-}) has been shown to stabilize the prolate, high-orbital-angular-momentum states of an Er^{3+} ion. Strikingly, of magnetically characterized Er^{3+} complexes, those with an Er–COT motif exhibit stronger SMM behavior than all those lacking it.[13] While computational models are required to explain many of the subtleties,[14] the Er–COT molecular subunit offers a general synthetic starting point with reliable anisotropy. Importantly, this allows the creation of clusters that can maintain high anisotropy while leaving available coordination sites for bridging ligands. Herein we employ the anisotropy-generating effects of COT^{2-} to synthesize a dinuclear Er complex, $[Er(\mu_2\text{-}Cl)(COT)(THF)]_2$ (**1**, Fig. 1). The combined effects of anisotropy and magnetic coupling give this complex the highest barrier to thermal spin relaxation for a ferromagnetically-coupled Er^{3+} complex and negate the need for a supplemental dc field to observe slow relaxation of the magnetization.

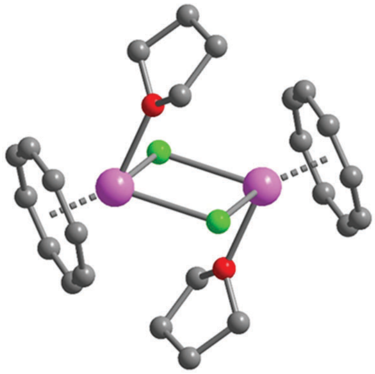

Fig. 1 Solid-state structure of **1** with spheres representing Er (pink), Cl (green), O (red), and C (gray). Hydrogen atoms have been omitted for clarity. The Er–Cl, Er–COT (centroid), Er–O distances are 2.7014(2)/2.7046(2) Å, 1.7538(1) Å, and 2.3367(1) Å, respectively. The Er–Er separation in this complex is 4.0809(2) Å.

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Synthesis of **1** proceeds through room temperature addition of K_2COT to anhydrous $ErCl_3$ in THF. After removal of KCl, pink crystals of **1** (48.2% yield) were obtained from a concentrated THF solution *via* vapor diffusion of diethyl ether. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ (no. 14) containing only the dinuclear complex as the repeat unit (Fig. 1 and Fig. S1, ESI†). The Er–Er midpoint defines the crystallographic inversion center and thus the crystal field environment of each Er^{3+} is equivalent. Analogues of this structural motif are known for the lighter lanthanides Ce, Pr, Nd, and Sm.[15] In these complexes, however, two THF molecules coordinate each metal center due to the larger ionic radii of the early lanthanides.

The dc magnetic susceptibility for **1** (Fig. 2) was measured between 2 and 300 K under a 1000 Oe applied field. At 300 K, $\chi_M T$ = 22.98 emu K mol^{-1}, nearly identical to the theoretical value of $\chi_M T$ = 22.96 emu K mol^{-1} for two uncoupled Er^{3+} centers ($M_J = 15/2$, $g = 6/5$). Upon cooling from 300 to 20 K, $\chi_M T$ declines to a local minimum of 20.2 emu K mol^{-1}, as expected for a thermal depopulation of the crystal-field split M_J manifold. Upon further cooling, $\chi_M T$ shows a smooth increase to a maximum of 23.5 emu K mol^{-1} at 1.9 K. This increase in $\chi_M T$ indicates an intramolecular Er^{3+} interaction that is predominantly ferromagnetic in nature. Ferromagnetic interactions are relatively uncommon in molecular lanthanide systems. Indeed, this marks the first Er–COT complex to show such an interaction – an important step in the design of stronger, multinuclear erbium-based SMMs. The final feature evident in the $\chi_M T$ data is a drop to 22.7 emu K mol^{-1} between 1.9 and 1.8 K. This drop can be indicative of further crystal field state depopulation or of magnetic blocking behavior indicative of a SMM. To test for SMM behavior we performed a field-cooled $\chi_M T$ measurement that yielded a non-superimposable curve thus confirming that, on the time-scale of the dc susceptibility measurement, we observe magnetic blocking below 2.4 K.

To gain more quantitative information about the magnetic dynamics of **1**, an ac magnetic susceptibility study was performed between 6 and 13 K. These measurements were acquired under zero bias field and a 4 Oe switching field in half-Kelvin temperature increments. The relaxation time, τ, was extracted from these data by simultaneously fitting the in-phase (χ') and out-of-phase (χ'') contributions to the ac susceptibility using a generalized Debye equation (Fig. 3 top and Fig. S3, ESI†).[3] Importantly, only one relaxation time is observed over three orders of magnitude in ac frequency, indicating a single magnetic relaxation pathway, consistent with the crystallographically aligned Er^{3+} ions.

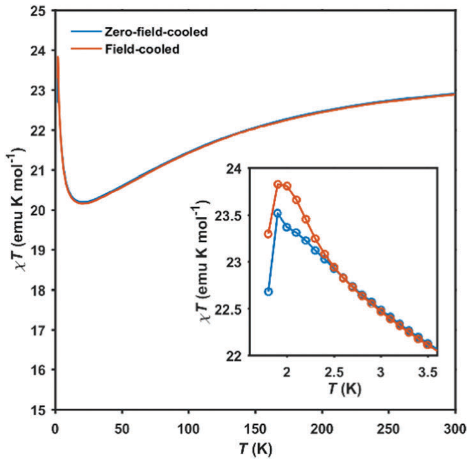

Fig. 2 Temperature dependence of magnetic susceptibility times temperature ($\chi_M T$ *vs.* *T*) for **1**. Inset: Divergence of field cooled and zero-field cooled susceptibility below 2.4 K.

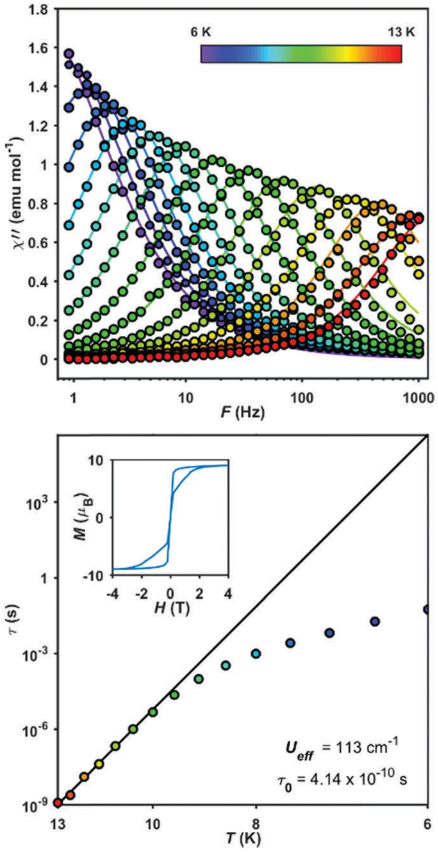

Fig. 3 (top) Out-of-phase component of the ac magnetic susceptibility of 1 between 6 and 13 K under zero bias field. Solid lines represent fits to the data. (bottom) Arrhenius plot of the temperature dependence of magnetic relaxation times (colored circles) for 1 and linear fit (black line) to Arrhenius law. Inset: Magnetization *versus* field at 1.8 K showing butterfly hysteretic behavior with a closed loop at zero field.

A plot of the fitted relaxation times *versus* temperature clearly shows two regimes of relaxation processes (Fig. 3, bottom). At temperatures between 10.5 and 13 K, $\ln(\tau)$ decreases linearly with $1/T$, indicating a thermally activated (Orbach) relaxation mechanism. Fitting these relaxation times to the Arrhenius equation yields an effective barrier height U_{eff} = 113 cm^{-1} and an attempt time of $\tau_0 = 4.1 \times 10^{-10}$ s. The magnitude of τ_0 points to a SMM operating under a fully thermally-activated relaxation mechanism. Below 10.5 K the relaxation times begin to show sublinear deviations from Arrhenius behavior, indicative of the dominant relaxation mode switching to quantum tunnelling of the magnetization.

To better understand the long timescale behavior, isothermal magnetization measurements were collected between 1.8 and

300 K in dc magnetic fields ranging from −7 to 7 T (Fig. 3 inset and Fig. S2, ESI†). At 1.8 K, the magnetic moment rises quickly to reach a near-saturation value of 9.35 μ_B by ∼3 T. As the field is lowered back to $H = 0$, magnetic hysteresis is observed; however, a precipitous zero-field drop occurs such that remnant magnetization is not observed ($M_r = 0\ \mu_B\ \text{mol}^{-1}$) on the timescale of the dc magnetization measurement. Although **1** shows no coercivity above 1.8 K, butterfly hysteresis is observed below 4.0 K, consistent with the divergence of field-cooled and zero-field cooled magnetic susceptibility measurements. The lack of measurable M_r is a common occurrence in SMMs. The value of M_r can often be increased through magnetically diluting the complex in a diamagnetic host lattice. This does not, however, alter the intrinsic properties of the molecule being studied, only lessens the convoluting effects of dipolar fields.

In summary, we have reported the synthesis and characterization of a dinuclear Er^{3+} complex incorporating COT^{2-} ligands. Complex **1** demonstrates the retention of single-ion anisotropy in a non-axial environment and ferromagnetic coupling through chloride ion bridges. These factors create slow magnetic relaxation with an effective barrier height of $U_{\text{eff}} = 113\ \text{cm}^{-1}$. This finding is rationalized by the idea that the halo-like COT^{2-} ligand is, quite generally, effective at stabilizing the prolate $M_J = 15/2$ state of the Er^{3+} ion, while allowing open coordination sites for bridging ligands to bind for the formation of multinuclear clusters. The absence of an open magnetic hysteresis loop indicates that further improvements can be made to the coupling strength and cluster nuclearity that will enhance both U_{eff} and the temperature at which magnetic hysteresis is observed while maintaining the strong anisotropy of the Er^{3+} ion.

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