Strong exchange and magnetic blocking in N₂³⁻-radical-bridged lanthanide complexes

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Single-molecule magnets approach the ultimate size limit for spin-based devices. These complexes can retain spin information over long periods of time at low temperature, suggesting possible applications in high-density information storage, quantum computing and spintronics. Notably, the success of most such applications hinges upon raising the inherent molecular spin-inversion barrier. Although recent advances have shown the viability of lanthanide-containing complexes in generating large barriers, weak or non-existent magnetic exchange coupling allows fast relaxation pathways that mitigate the full potential of these species. Here, we show that the diffuse spin of an N₂³⁻ radical bridge can lead to exceptionally strong magnetic exchange in dinuclear Ln(III) (Ln = Gd, Dy) complexes. The Gd(III) congener exhibits the strongest magnetic coupling yet observed for that ion, while incorporation of the high-anisotropy Dy(III) ion gives rise to a molecule with a record magnetic blocking temperature of 8.3 K at a sweep rate of 0.08 T s⁻¹.

Nearly twenty years ago, it was discovered that molecules can possess a substantial energy barrier to inversion of their total spin S, enabling them to behave like nanoscopic classical magnets, as demonstrated by the observation of magnetic hysteresis at low temperature[1]. Since then, numerous experimental and theoretical studies, mostly on manganese-oxo clusters, have explored the parameters that govern the spin-reversal barriers in such single-molecule magnets[2]. Although increasing S or the axial anisotropy D can augment the spin-reversal barrier ($U = S^2|D|$) for a molecule, efforts to increase these parameters simultaneously are complicated by their interrelationship[3,4]. Clusters with many exchange-coupled transition metal centres can have extremely large S values[5], but the accompanying D values tend to be low, counterbalancing any anticipated enhancement in spin-reversal barrier. This caveat has been a crucial roadblock to the promise of single-molecule magnet-based devices[6–10].

The foregoing observation has led some researchers to focus on small, high-anisotropy molecules containing several, or even just one, spin carrier[11–14]. The lanthanides and actinides are particularly well suited for this, because their large unquenched orbital moments and strong spin–orbit coupling can produce single-ion anisotropies that are unparalleled in the periodic table. In particular, one area of attention is the synthesis of dysprosium-containing molecules, which benefit from both the high moment and the high anisotropy of the spin–orbit coupled Dy(III) Kramers doublet ground state ($S = 5/2$, $L = 5$, $J = 15/2$). Indeed, research on dysprosium complexes has yielded a flood of groundbreaking results[15,16], including the highest relaxation energy barriers for multinuclear clusters[17–19] and the highest temperature at which hysteresis has been observed for any single-molecule magnet[17]. Importantly, the cluster molecules provide little to no evidence for magnetic coupling between Dy(III) centres owing to the limited radial extension of the 4f orbitals, and the relaxation barrier is probably attributable to the individual Dy(III) ions. This effect limits the maximum spin-reversal barrier that can be achieved in lanthanide-containing complexes, because the moment is restricted to that of a single ion. Moreover, exchange coupling has been found to mitigate quantum tunnelling relaxation processes that lead to the loss of remnant magnetization

under zero applied field[20]. Accordingly, with no exchange coupling, the molecule displaying the highest measured barrier, 230 cm⁻¹ for [TbPc₂]⁻ (H₂Pc = phthalocyanine) shows deviations from thermally activated behaviour at such a high temperature that only a very small remnant magnetization is apparent in its hysteresis loop, and then only at 1.7 K (ref. 12).

Results and discussion

Lanthanide-containing complexes exhibiting both high anisotropy and strong exchange coupling present a promising route towards single-molecule magnets with high blocking temperatures. One means of achieving strong coupling is through the use of radical bridging ligands with diffuse spin orbitals that can penetrate the core electron density of the lanthanide ions, where the 4f spin orbitals lie deeply buried. We therefore chose to probe the magnetism of two N₂³⁻-radical-bridged dilanthanide complexes, as isolated in [K(18-crown-6)]{[(Me₃Si)₂N]₂(THF)Ln}₂(μ-η^2:η^2-N₂) (Ln = Gd (**1**), Dy (**2**); THF, tetrahydrofuran). Compound **1** indeed exhibits much stronger magnetic coupling than previously obtained for a Gd(III) compound, and the combination of strong coupling and high anisotropy in **2** leads to the highest magnetic blocking temperature yet observed for a single-molecule magnet.

Compounds **1** and **2** are readily generated through reduction of the N₂²⁻-bridged complexes {[(Me₃Si)₂N]₂(THF)Ln}₂(μ-η^2:η^2-N₂) (Ln = Gd (**3**), Dy (**4**)) with potassium graphite in THF. The resulting compounds are isostructural, with the dinuclear lanthanide complexes residing on inversion centres, which render the two metal ions equivalent by symmetry (Fig. 1). The coordination environment of each lanthanide is pseudotetrahedral, with one vertex being occupied by the bridging N₂³⁻ ligand. The radical nature of the N₂³⁻ unit in such species was confirmed by means of a battery of techniques, including single-crystal X-ray diffraction, electron paramagnetic resonance, and infrared and Raman spectroscopy, as performed on an isostructural Y(III) analogue reported previously[21]. This assignment was further corroborated by electronic structure calculations, which showed the N₂³⁻ unit to have a singly occupied π^* orbital oriented perpendicular to the Ln–N₂–Ln plane. Significantly, the diffuse character of the orbital,

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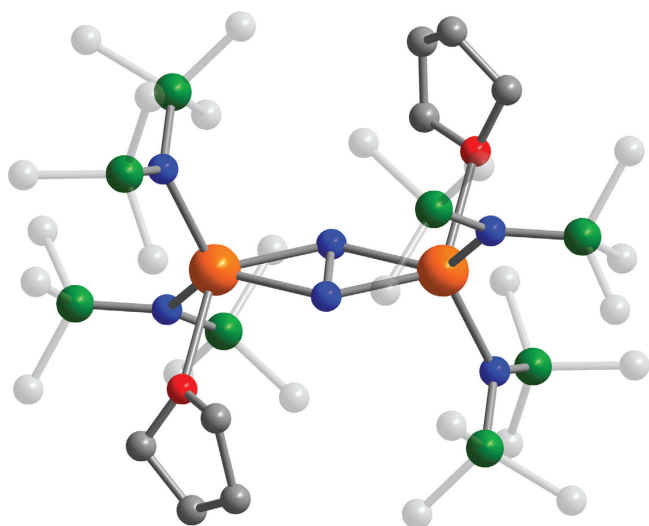
Figure 1 | Structure of the centrosymmetric [{[(Me$_3$Si)$_2$N]$_2$Gd(THF)}$_2$(μ-η^2:η^2-N$_2$)]$^-$ anion, as crystallized in compound 1. Orange, Gd; green, Si; grey, C; blue, N; red, O. H atoms are omitted and methyl groups are faded for clarity. Complexes **2**, **3** and **4** exhibit analogous structures. Selected interatomic distances (Å) for **1–4**, respectively: N−N = 1.401(4), 1.399(2), 1.278(4), 1.305(6); mean Ln−N(N$_2^{3-}$) = 2.236(2), 2.208(1), 2.340(2), 2.300(3); mean Ln−N(N[SiMe$_3$]$_2$) = 2.370(2), 2.329(1), 2.287(2), 2.259(2); Ln−O = 2.480(2), 2.455(1), 2.441(2), 2.405(2); Ln···Ln = 4.2483(3), 4.1878(2), 4.5008(7), 4.4099(3).

stemming from electron–electron repulsions associated with the formal 3− charge of the bridging ligand, can be expected to enhance exchange coupling with the lanthanide centres.

Owing to their half-filled f-electron valence shell, Gd(III) compounds offer a unique platform among the Ln(III) ions for studying magnetic exchange coupling, because the orbital singlet results in magnetic behaviour that is not complicated by the effects of spin–orbit coupling. This behaviour lends itself to a 'spin-only' analysis similar to that used for most transition metals, where the orbital moment is generally quenched by the ligand field environment. To probe the magnetic coupling in the N$_2^{3-}$-radical-bridged digadolinium complex of **1**, direct current (d.c.) magnetic susceptibility (χ_M) data (the propensity of the complex to be magnetized under an external magnetic field) were collected in the temperature range 2–300 K (Fig. 2a). At 300 K, the $\chi_M T$ value is 15.25 emu K mol^{-1} (emu = electromagnetic units), which is lower than the value expected ($\chi_M T = 16.13$ emu K mol^{-1}) for two magnetically isolated $S = 7/2$ Gd(III) ions and a single radical $S = \frac{1}{2}$ N$_2^{3-}$ unit. This low moment already suggests the presence of appreciable antiferromagnetic coupling within the complex, even at room temperature. As the temperature drops, $\chi_M T$ rises to a maximum value of 23.83 emu K mol^{-1} at 9 K, approaching the value of 24.38 emu K mol^{-1} expected for an $S = 13/2$ ground state arising from antiferromagnetic coupling between the radical and the two Gd(III) ions.

To quantify this effect, the data were fit using a spin-only Hamiltonian, $\hat{H} = -2J\hat{S}_{radical} \cdot (\hat{S}_{Gd(1)} + \hat{S}_{Gd(2)}) - zJ'\langle S_z\rangle S_z$, which models both the intramolecular coupling (J, coupling constant; $\hat{S}$, spin operator for each paramagnetic centre) and a weak intermolecular interaction (z, number of nearest-neighbour molecules; J', intermolecular coupling constant; $\langle S_z\rangle$, mean value of the S_z component of the spin operator). The model provides a good fit to the data, revealing parameters of $J = -27$ cm^{-1} and $J' = 0.07$ cm^{-1}. Notably, this value of J represents the strongest coupling, ferromagnetic or antiferromagnetic, observed for a gadolinium compound. Although Gd(III) complexes typically show

exchange constants of less than 3 cm^{-1} (ref. 22), the previous records of 6 and 5 cm^{-1} were achieved in the compounds [(Tp)$_2$Gd(dtbsq)] (Tp$^-$ = hydrotris(pyrazolylborate); dtbsq$^-$ = 3,5-di-$tert$-butylsemiquinonato) and [L^{1}CuCl$_2$Gd(H$_2$O)$_4$]Cl (L^{1}H$_2$ = 1,3-bis((3-methoxysalicylidene)amino)-2,2'-dimethylpropane), respectively[23,24].

The unprecedented strength of the coupling in **1** indicates that the diffuse N$_2^{3-}$-radical spin orbital creates an unusually effective direct exchange pathway, despite the contracted nature of the Gd(III) 4f orbitals. To check whether the radical bridge is essential for attaining strong coupling in this system, the magnetic properties of the non-radical N$_2^{2-}$-bridged analogue **3** were also investigated. Note that, although the reduced charge of the bridging unit results in a slight geometric difference, with the N atoms 0.12 Å closer together and the Gd atoms 0.25 Å further apart, this compound represents the closest non-radical-bridged analogue available for comparison. As shown in Fig. 2a, $\chi_M T$ for compound **3** decreases gradually as the temperature is lowered, indicating the presence of only very weak antiferromagnetic coupling. Here, using the Hamiltonian $\hat{H} = -2J\hat{S}_{Gd(1)} \cdot \hat{S}_{Gd(2)}$ provides a coupling constant of $J = -0.49$ cm^{-1}. With a magnitude more than 50 times
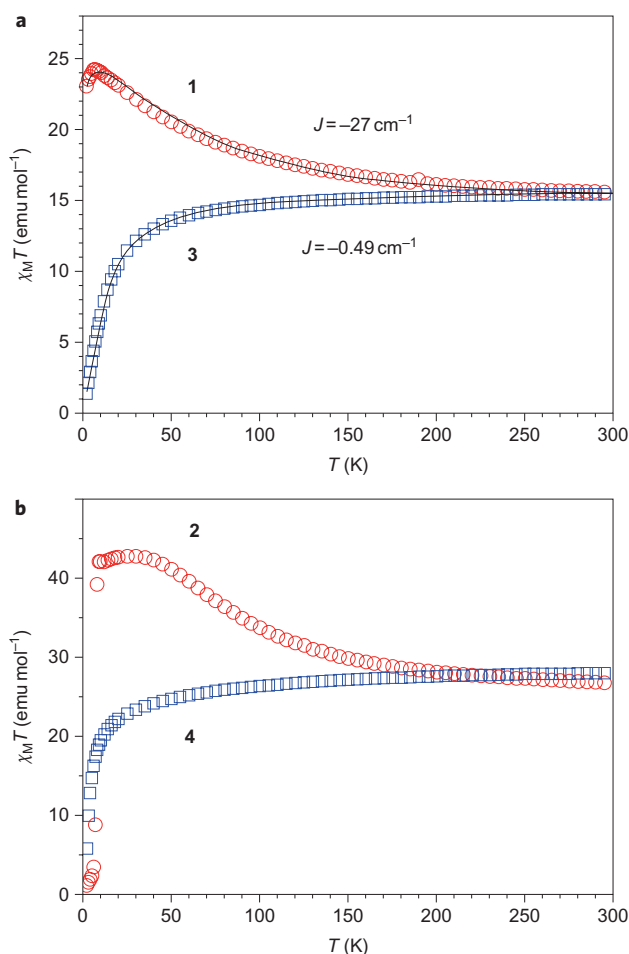

Figure 2 | Variable-temperature molar magnetic susceptibility data (χ_M). **a**, Data for Gd(III) compounds **1** and **3**. The $\chi_M T$ data for **1** (red circles) deviate from those of **3** (blue squares) at a high temperature, indicating a significant difference in their magnetic coupling due to the presence or absence of the radical N$_2^{3-}$ bridging ligand. This difference is quantified by spin Hamiltonians described in the text. **b**, Data for Dy(III) compounds **2** and **4**. Although fitting of the data is not possible as in **a**, the drastic difference in the curvature between **2** (red circles) and **4** (blue squares) mirrors the behaviour in **1** and **3**, and may indicate similar trends in their magnetic coupling.

weaker than that observed in **1**, coupling between two lanthanide ions via superexchange is clearly extremely weak, even through such a compact diamagnetic bridging ligand as N_2^{2-}. These results demonstrate the ability of the N_2^{3-} radical ligand to mediate strong magnetic exchange coupling between lanthanide ions, and highlight the promise of other radical bridging ligands for inducing similar behaviour.

Although the presence of isotropic Gd(III) ions in **1** enables a straightforward analysis of the magnetic exchange, the lack of anisotropy precludes single-molecule magnet behaviour. In view of this, we chose to investigate compound **2**, in which the Gd(III) ions are replaced by two high-anisotropy Dy(III) ions. To start, d.c. magnetic susceptibility data were collected in the temperature range 2–300 K (Fig. 2b). Analogous to the behaviour observed for **1**, at 300 K, the $\chi_M T$ for **2** (26.65 emu K mol^{-1}) is significantly lower than the value of 28.71 emu K mol^{-1} expected for two magnetically isolated $J = 15/2$ Dy(III) ions and a single radical $S = 1/2$ N_2^{3-} unit. However, owing to the complex interaction of the spin–orbit coupled ground state with the ligand field environment, conclusions about the magnetic coupling are not as readily drawn from the $\chi_M T$ data as they were for **1**. In Dy(III)-containing compounds, the weak crystal field induces an energy splitting of the total angular momentum projections (m_J) that comprise the J ground state. Progressive depopulation of these states results in a decline in the magnetic moment with decreasing temperature, and thus it is impossible to deconvolute changes in $\chi_M T$ resulting from thermal depopulation of m_J levels and those resulting from magnetic coupling without an exhaustive knowledge of the electronic structure. In **2**, however, $\chi_M T$ actually increases with decreasing temperature, reaching a maximum of $\chi_M T = 42.54$ emu K mol^{-1} at 25 K. This rise in $\chi_M T$ for a lanthanide system having an unquenched orbital moment has not previously been observed in molecular magnetism, and offers evidence that the strong magnetic exchange coupling apparent in **1** is also present in **2**.

To confirm that the unusual magnetic behaviour of **2** is indeed associated with strong coupling through the radical bridge, the magnetic properties of the non-radical N_2^{2-}-bridged analogue **4** were probed. As expected, the $\chi_M T$ data for **4** show the normal decline in moment with decreasing temperature common to lanthanides with an unquenched orbital moment (Fig. 2b). The stark contrast between the susceptibility behaviours of **2** and **4** further demonstrates the effectiveness of the N_2^{3-} radical in facilitating extraordinarily strong magnetic coupling.

At very low temperatures, the behaviour of **2** shows important differences from that of **1** (Fig. 2). As the temperature is lowered below 25 K, $\chi_M T$ gradually declines before suddenly plummeting, below 10 K, to a near constant value of ~2 emu K mol^{-1}. This sudden decrease in moment may be indicative of blocking of the magnetic moment and therefore single-molecule magnet behaviour. To investigate this possibility, variable-frequency alternating current (a.c.) magnetic susceptibility measurements were performed. In the temperature range 10–20 K, the decline in the in-phase (χ', Fig. 3a) component of the a.c. susceptibility of **2**, concomitant with the appearance of peaks in the out-of-phase (χ'', Fig. 3b) component, clearly indicate slow magnetic relaxation. To quantify this effect, the data were fit using a generalized Debye equation to extract relaxation times, and an Arrhenius plot was constructed to study the temperature dependence of the magnetic relaxation (Fig. 3c). As expected for a single-molecule magnet, the relaxation times exhibit an exponential dependence on temperature, and an Arrhenius fit to the data gives an effective relaxation barrier of $U_{eff} = 123$ cm^{-1} with a pre-exponential factor of $\tau_0 = 8 \times 10^{-9}$ s. Importantly, this barrier is the largest yet reported for an exchange-coupled cluster, nearly doubling the previous mark of 67 cm^{-1} observed for a dinuclear Co-carbene complex[25]. Attempts to study the relaxation at lower temperatures using time-dependent decay of the magnetization have so far
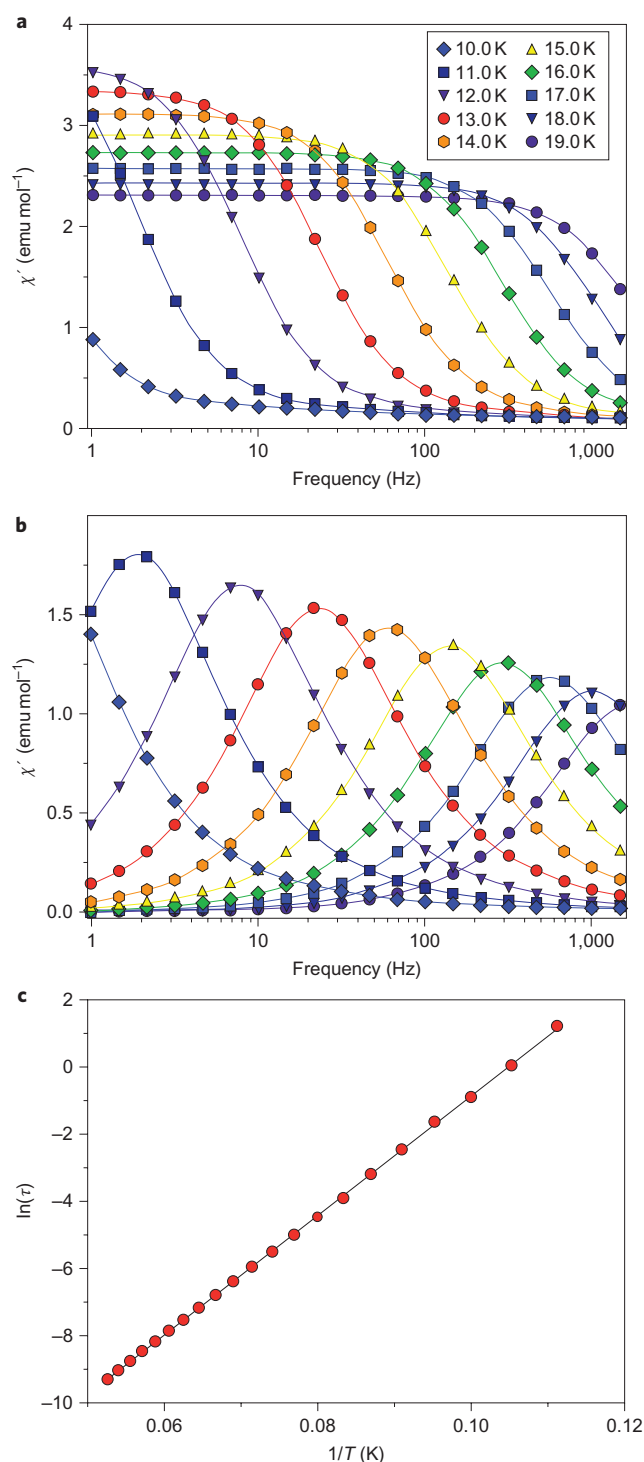

Figure 3 | Dynamic magnetic data for 2. a,b, Temperature dependence of the in-phase (χ'_M, **a**) and out-of-phase (χ''_M, **b**) components of the a.c. magnetic susceptibility for **2** under zero applied d.c. field. A non-zero out-of-phase component to the susceptibility indicates the presence of slow magnetic relaxation. Relaxation times are extracted from fits of χ'_M and χ''_M to a generalized Debye equation. **c,** Plot of inverse temperature versus the natural log of the relaxation time. Standard deviations of the relaxation times are determined from a nonlinear least-squares analysis using the program SolverAid (Version 7) by R. de Levie (Microsoft Excel Macro 2007); error bars are not shown as they lie within the radius of the symbols. The black line corresponds to a fit to the Arrhenius expression for the relaxation time $\tau = \tau_0 \exp(U_{eff}/k_B T)$, affording $U_{eff} = 123$ cm^{-1} (178 K) and $\tau_0 = 8 \times 10^{-9}$ s with $R^2 = 0.999$.
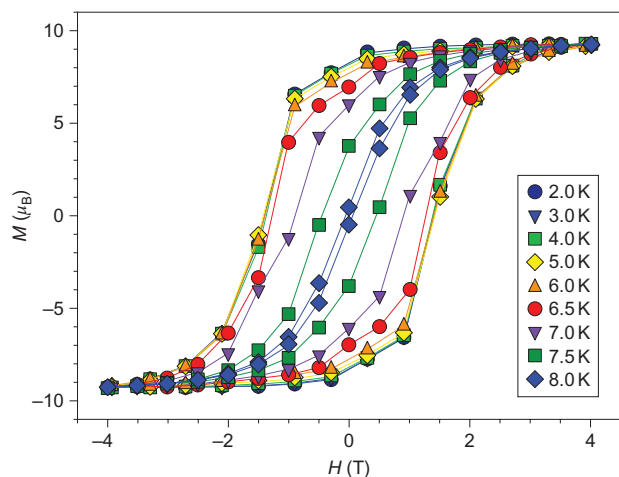
Figure 4 | Magnetization (*M*) versus d.c. magnetic field (*H*) for 2.
Magnetization data were collected while sweeping the magnetic field at an average sweep rate of 0.08 T s^{-1}. Solid lines are guides for the eye. As the magnetic field is swept from 4 to −4 T and back, hysteretic behaviour is clearly observed, indicating slow magnetic relaxation on the timescale of the measurement. Open magnetic hysteresis loops are observed for all data from 2.0 to 8.0 K. Supplementary Fig. S8 shows that the hysteresis loop remains open until 8.3 K.

been unsuccessful, probably due to strong magnetic avalanche effects created by rapid removal of the d.c. magnetic field (Supplementary Fig. S3).

Recently, other multidysprosium complexes have been shown to exhibit slow magnetic relaxation, with the highest barrier recently reported as 139 cm^{-1} (ref. 19). However, the behaviour of these compounds appears to arise largely from the strong anisotropy of the Dy(III) ions with only weak contributions from intramolecular exchange coupling. This often results in distinct relaxation processes that can be correlated to the different crystal field environments for crystallographically independent Dy(III) ions[17,18]. Most importantly, despite the seemingly high energy barriers to spin inversion, the anisotropy in such compounds typically leads to alternative relaxation pathways that shortcut the barrier and drastically reduce the actual relaxation time. For example, the cluster Dy$_4$L$_4$(MeOH)$_6$ (H$_3$L = [(2-hydroxy-3-methoxyphenyl)methylene]hydrazide) has a relaxation barrier of 120 cm^{-1}, but deviations from Arrhenius behaviour are observed below 20 K, where the relaxation time is only 0.001 s (ref. 18). This means that the relaxation time at 7 K is on the order of tenths of a second, orders of magnitude shorter than the expected time of ∼2 h.

The strong magnetic coupling in **2** suggests that slow magnetic relaxation arises through a 'giant spin' mechanism, in which the coupled Dy(III)-radical system operates as a single magnetic unit. Indeed, this is consistent with the relatively broad temperature range over which Arrhenius activation behaviour persists. To test the assumption that the strong coupling in **2** is responsible for its single-molecule magnet behaviour instead of just isolated single-ion anisotropy, the frequency-dependent a.c. susceptibility of the non-radical N$_2$$^{2-}$-bridged analogue **4** was measured. Here, an out-of-phase signal is clearly observed (Supplementary Fig. S4); however, the anisotropy barrier is drastically reduced to 18 cm^{-1} with a τ_0 value of 2 × 10^{-6} s. The value of the time constant τ_0 is large for a single-molecule magnet, similar to many single-ion systems that have been previously studied. Additionally, **4** displays a nearly constant low-temperature relaxation time indicating a strong, non-thermally activated relaxation process (Supplementary Fig. S7). All of these properties indicate that **4**, with very weakly coupled Dy(III) ions, behaves analogously to single-ion

single-molecule magnets, where the anisotropy barrier is derived from the nearly isolated ground states of the Dy(III) ions. This provides still further evidence that **2** generates its anisotropy from a concerted effect of the anisotropic Dy(III) ground states and the strong magnetic coupling through the radical N$_2$$^{3-}$ bridge.

To confirm unequivocally the magnet-like behaviour of **2**, variable-field magnetization measurements were performed (Fig. 4). Remarkably, magnetic hysteresis is observed at temperatures up to 8.3 K using sweep rates accessible with a conventional magnetometer. This means that a remnant magnetization can be observed on the timescale of minutes at a temperature higher than any yet recorded for a molecular species. Applying a sweep rate of 0.08 T s^{-1}, the hysteresis loop remains virtually unchanged from 2 to 6 K, with a coercive field of $H_c \approx 1.5$ T and a remnant magnetization of $M_r \approx 8.9\mu_B$. Above this temperature, the coercive field begins to drop, eventually reaching ∼20 Oe at 8.3 K (0.02 T s^{-1}) (Supplementary Fig. S8) before the loop completely closes. Although it can be difficult to compare hysteresis data between compounds because they are so strongly dependent on the sweep rates and the fields selected, compound **2** represents a new benchmark when compared to the transition-metal cluster record of 4.5 K (0.14 T s^{-1})[26], the dysprosium cluster record of 7 K (0.14 T s^{-1})[17] and the single-ion single-molecule magnet record of 4 K (no sweep rate given) for [Dy(Pc(OEt)$_8$)$_2$](SbCl$_6$) (ref. 15). Indeed, **2** represents the strongest magnet-like behaviour yet observed for a molecule (Supplementary Fig. S10).

Conclusion

Our results demonstrate that strong magnetic coupling combined with *f*-element single-ion anisotropy gives rise to a new record single-molecule magnet, which exhibits magnetic hysteresis up to 8.3 K at conventional sweep rates. Future efforts will focus on extending this system to other radical bridging ligands and other lanthanide ions, as well as on developing synthetic methods for generating radical-bridged clusters with more than two lanthanide ions. It is hoped that the principles uncovered here may ultimately lead to single-molecule magnets with significantly higher relaxation barriers capable of retaining their magnetization at more practical temperatures.

Methods

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Author contributions

W.J.E. and M.F. designed and executed the synthesis and crystallographic characterization of all compounds. J.R.L. and J.D.R. planned and executed the magnetic measurements and analysed the resulting data. All authors were involved in the writing of the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/naturechemistry. Reprints and permission information is available online at http://www.nature.com/reprints/. Correspondence and requests for materials should be addressed to W.J.E. and J.R.L.