We report the first near-linear bis(amide) 4f-block compound and show that this novel structure, if implemented with dysprosium(III), would have unprecedented single molecule magnet (SMM) properties with an energy barrier, $U_{\text{eff}}$, for reorientation of magnetization of 1800 cm$^{-1}$.

Since their initial discovery, single molecule magnets (SMMs) have been lauded as candidates for high density data storage devices. A major breakthrough in the field occurred in 2003 with the observation of SMM behavior in a monometallic $\{\text{TbPc}_2\}$-complex with an energy barrier, $U_{\text{eff}} = 230$ cm$^{-1}$. The ensuing decade saw rapid growth in lanthanide SMMs with the $U_{\text{eff}}$ barrier to magnetization reversal increased to 652 cm$^{-1}$ for another derivative of $\{\text{TbPc}_2\}$, and 585 cm$^{-1}$ for a polymetallic Dy@$\{\text{Y}_4\text{K}_2\}$ complex. The highest blocking temperature $T_B$ (i.e. the temperature at which hysteresis is observed) was also increased to 14 K, via an N$_2$-radical bridge in a $\{\text{ TbN}_2\}$ complex.

Although three of these milestones employ the TbIII ion, by far the most utilized lanthanide ion in SMMs is DyIII by virtue of its unique electronic structure. Apart from a radical-bridged $\{\text{ Dy}_2\text{N}_2\}$ complex, nearly all polymetallic DyIII-based SMMs possess negligible interactions between magnetic spin centres, and instead rely on the single ion anisotropy of DyIII ($\approx$ 3900 cm$^{-1}$) to provide the barrier to the reversal of magnetization. Intra- or intermolecular interactions are often detrimental to the performance of DyIII SMMs so that doping a single, unique quantization axis for the total angular momentum $m_I$ states.

The simplest axial ligand environment is a linear two-coordinate complex with donor atoms exclusively on a single Cartesian axis; the $U_{\text{eff}}$ barrier is so large for the $\{\text{Dy}_5\}$ and $\{\text{Dy}_4\text{K}_2\}$ alkoxide complexes because of the strongly axially repulsive crystal field potentials along the local z-direction of each DyIII. Other compounds such as $\{\text{C}_6\text{H}_6\text{Lu}\}$ (ref. 15) or Cloke’s bis(arene) lanthanide complexes are sometimes described as linear, but lack donor atoms directly on the axis. Linear 3d-metal compounds also show remarkable magnetic behaviour with very high $U_{\text{eff}}$ values. A one coordinate lanthanide complex $\{\text{DyO}^+\}$ has been considered theoretically with a very large $U_{\text{eff}}$ predicted, however such an entity is not chemically feasible.

Very low coordination numbers for 4f-ions are difficult to achieve as these are large, electropositive ions, which require a sterically demanding ligand. Such a pro-ligand HN(SiPr$_3$)$_2$, was designed, and synthesised from C$_3$H$_7$SiPr$_3$ and LiHN(SiPr$_3$)$_2$, and this was converted to the group 1 transfer agent [KN(SiPr$_3$)$_2$] with KH. Reacting two equivalents of [KN(SiPr$_3$)$_2$] with samarium(ii) dioxido yields the mononuclear homoleptic bis(amide) complex, [(Pr$_3$Si)$_2$N–Sm–N(SiPr$_3$)$_2$] (Fig. 1, see ESI† for details).

Complex 1 is the first near-linear f-element complex, with an N–Sm–N angle of 175.52(18)° in the solid state (Fig. 2, see ESI† for details); this near-linearity contrasts with the bent C–Ln–C angles of [Ln$^{II}$(C(SiMe$_3$)$_2$)$_2$] complexes (Ln = Sm, Yb, Eu).
bulky tBu groups are vital for the isolation of a homoleptic complex, as [Sm[N(SiMe₃)₂]₂(THF)]₂ exhibits additional O-donors.21 The Sm–N distances in [Sm{N(SiMe₃)₂}₂(THF)]₂ are staggered with respect to each other (twist angle of 44.42°), giving the most energetic Kramers doublet a large 15/2 perpendicular to the main magnetic axis.14 Along the main magnetic axis the almost pure 15/2 state and only includes pathways which reverse the magnetization. Relaxation probabilities are calculated based on a magnetic perturbation and are normalized from each departing state (see ESI† for details).}

Such a Dy III compound is challenging to make; we believe a DyIII and produce monstrous uniaxial magnetic anisotropy. Such a Dy III compound is challenging to make; we believe a


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Fig. 2 Molecular structure of 1. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sm1–N1 2.483(6), Sm1–N2 2.483(6), Sm1–C7 3.180(8), Sm1–C16 3.169(8), Sm1–C19 3.082(8), Sm1–C34 3.224(8), N1–Sm1–N2 175.52(18), Sm1–N1–Si1 109.9(3), Sm1–N1–Si2 111.6(3), Si1–N1–Si2 138.5(4), Sm1–N2–Si3 109.8(4), Sm1–N2–Si4 110.8(3), Si3–N2–Si4 138.8(4).

Fig. 3 Electronic states and magnetic transition probabilities for the ground 4H₁₅/₂ multiplet of 2 in zero field. The x-axis shows the magnetic moment of each state along the main magnetic axis of the molecule. Relaxation commences from the −15/2 state and only includes pathways which reverse the magnetization. Relaxation probabilities are calculated based on a magnetic perturbation and are normalized from each departing state (see ESI† for details).
g-factors above a certain threshold or where its main magnetic axis is non-collinear with that of the ground state. All non-QTM transitions are induced by the vibrational modes of the lattice (phonons) which create local oscillating magnetic fields through modulation of dipolar fields as well as an oscillating crystal field potential.13 To a first approximation, we can associate the probability of a phonon induced transition with the average magnetic3,14,24 and crystal field perturbation matrix elements (see ESI† for details).

Compared to all known DyIII complexes the calculated properties for 2 are unique with very small transverse g-factors and a common principal axis for the lowest six Kramers doublets. This suggests that both the probability of QTM within the ground doublet and TA-QTM is vanishingly small until the two most energetic doublets. Orbach relaxation is also strongly disfavoured in the low lying states as magnetic transition probabilities due to phonons are miniscule (Fig. 3). Efficient magnetic relaxation will only occur via the highest energy doublets (Fig. 3, Fig. S4 and Tables S4 and S5, ESI†). Therefore the ab initio calculation predicts $U_{\text{eff}} \approx 1800 \text{ cm}^{-1}$ for 2 – far greater than any complex to date. Whilst such calculations may over-estimate the energies of the crystal field states,25,26 we can predict a $T_{\text{B}}$ in excess of 77 K as such temperatures are often around 1/20th of the $U_{\text{eff}}$ value if QTM within the ground doublet is disfavored, e.g. the $T_{\text{B}}/U_{\text{eff}}$ ratios for $[\text{Tb}_2\text{N}_2(\text{H}_2\text{O})_3]$, $[\text{Mn}_{1/2}]^2$ and $[\text{Mn}]_0$ are approximately 1/16, 1/15 and 1/13 $\text{cm}^{-1}$ K$^{-1}$, respectively. Calculations for the TbIII analogue, which is also a 4f ion, predict analogous behavior to 2 (Table S6, ESI†). The high local symmetry at the DyIII site implies that the nuclear quadrupole and hyperfine interactions will be axially symmetric, preventing efficient QTM within the lower energy doublets.

To examine the stability of 2, we have performed ab initio calculations for modified geometries where the N–Dy–N angle and the Dy–N bond lengths have been altered by 0.5° and ±0.01 Å, respectively (Fig. S3, ESI†). The results show that 2 is stabilized when the Dy–N bond length is shortened and the N–Dy–N angle is closer to 180° compared to 1, yielding more favorable electronic properties. These calculations do not take into account the inclusion of a counter-ion in the structure, which may have consequences for crystal packing and the local structure of 2.

Compound 1 is the first near-linear bis[amido] 4f-block complex. It allows us to propose a blueprint for the first generation of high-temperature SMMs, with blocking temperatures exceeding that of liquid $\text{N}_2$ (77 K). The synthesis of the proposed archetype, viz. the DyIII and TbIII analogues of 1, is currently underway in our laboratory, however we believe this is a target many other groups should be pursuing. Calculations on other 4f ions suggest that 4f is ideal; even for the oblate 4f TbIII analogue, 4, we find that the pseudo-doublet shows strong mixing between the $|-m_f|$ and $|+m_f|$ projections (Tables S7 and S8, ESI†), which would lead to strong zero-field QTM. While 2 would have a huge $U_{\text{eff}}$, an even higher $U_{\text{eff}}$ barrier might be possible if dianionic monodentate ligands could be incorporated, e.g. $[\text{Pr}_2\text{Si}_2\text{C}(-\text{Dy})\text{C}(-\text{SiPr}_3)_2]$, containing dianionic methanediides. Our preliminary results suggest this could raise $U_{\text{eff}}$ by a factor of 1.2 to 1.3. The incredible advances made in low coordination number metal–organic compounds in the last decade suggest that such hypothetical complexes are now chemically feasible. These metal–organic compounds are becoming of great importance in molecular magnetism.27,28

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Notes and references