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The first near-linear bis(amide) f-block complex: a blueprint for a high temperature single molecule magnet†

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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_{eff} , for reorientation of magnetization of 1800 cm^{-1} .

Since their initial discovery,¹ single molecule magnets (SMMs) have been lauded as candidates for high density data storage devices.² A major breakthrough in the field³ occurred in 2003 with the observation of SMM behavior in a monometallic $\{\text{TbPc}_2\}^-$ complex with an energy barrier, $U_{\text{eff}} = 230 \text{ cm}^{-1}$.⁴ The ensuing decade saw rapid growth in lanthanide SMMs⁵ with the U_{eff} barrier to magnetization reversal increased to 652 cm^{-1} for another derivative of $\{\text{TbPc}_2\}$,⁶ and 585 cm^{-1} for a polymetallic $\text{Dy}@Y_4K_2\}$ complex.⁷ The highest blocking temperature T_B (*i.e.* the temperature at which hysteresis is observed) was also increased to 14 K, *via* an $\text{N}_2^{3-\bullet}$ radical bridge in a $\{\text{Tb}_2\text{N}_2^{3-\bullet}\}$ complex.⁸

Although three of these milestones employ the Tb^{III} ion, by far the most utilized lanthanide ion in SMMs is Dy^{III} by virtue of its unique electronic structure.⁹ Apart from a radical-bridged $\{\text{Dy}_2\text{N}_2^{3-\bullet}\}$ complex,¹⁰ nearly all polymetallic Dy^{III} -based SMMs possess negligible interactions between magnetic spin centres, and instead rely on the single ion anisotropy of Dy^{III} (*i.e.* the local crystal field environment) to provide the barrier to the reversal of magnetization. Intra- or intermolecular interactions are often detrimental to the performance of Dy^{III} SMMs so that doping a small amount of the paramagnetic ion into a diamagnetic host lattice (usually the Y^{III} analogue) often results in an increased U_{eff} .⁷

An electrostatic model for the design of ideal ligand environments to exploit the maximal anisotropy of Dy^{III} has been postulated,^{11,12} and shown to be in good agreement with multi-configurational complete active space Self consistent field

(CASSCF) *ab initio* calculations¹² that are often employed to examine 4f complexes, pioneered by Chibotaru.^{7,13} Electrostatic approaches suggest that the optimal ligand environment to exploit the oblate spheroidal electron density of Dy^{III} is axial, where rigorously axial systems have the benefit of maintaining a single, unique quantization axis for the total angular momentum m_j states.¹⁴ A set of unadulterated m_j states implies that the probability of quantum tunnelling of the magnetization (QTM) is reduced, therefore increasing magnetic relaxation times.²

The simplest axial ligand environment is a linear two-coordinate complex with donor atoms exclusively on a single Cartesian axis; the U_{eff} barrier is so large for the $\{\text{Dy}_5\}$ and $\{\text{Dy}_4\text{K}_2\}$ alkoxide complexes⁷ because of the strongly axially repulsive crystal field potentials along the local z -direction of each Dy^{III} . Other compounds such as $[(\text{C}_8\text{H}_8)_2\text{Ln}]^-$ (ref. 15) or Cloke's bis(arene) lanthanide complexes¹⁶ 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_{eff} values.¹⁷ A one coordinate lanthanide complex $[\text{DyO}]^+$ has been considered theoretically with a very large U_{eff} predicted,¹⁴ 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 $\text{HN}(\text{Si}^i\text{Pr}_3)_2$ was designed, and synthesised from ClSi^iPr_3 and $\text{LiHN}(\text{Si}^i\text{Pr}_3)_2$, and this was converted to the group 1 transfer agent $[\text{KN}(\text{Si}^i\text{Pr}_3)_2]$ with KH. Reacting two equivalents of $[\text{KN}(\text{Si}^i\text{Pr}_3)_2]$ with samarium(II) diiodide yields the mononuclear homoleptic bis(amide) complex, $[(^i\text{Pr}_3\text{Si})_2\text{N}-\text{Sm}-\text{N}(\text{Si}^i\text{Pr}_3)_2]$ **1** (Fig. 1, see ESI† for details).

Complex **1** is the first near-linear f-element complex, with an N–Sm–N angle of $175.52(18)^\circ$ in the solid state (Fig. 2, see ESI† for details); this near-linearity contrasts with the bent C–Ln–C angles of $[\text{Ln}^{\text{II}}\{\text{C}(\text{SiMe}_3)_3\}_2]$ complexes (Ln = Sm, Yb, Eu).^{18–20} The

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Fig. 1 Synthetic route to **1**.





Fig. 2 Molecular structure of **1**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^{\circ}$): 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).

bulky ^iPr groups are vital for the isolation of a homoleptic complex, as $[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ exhibits additional O-donors.²¹ The Sm–N distances in **1** [2.483(6) Å] are longer than those observed in $[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ [mean Sm–N 2.433(9) Å] but this is compensated by **1** exhibiting four short Sm...C_{methylene} distances [Sm...C 3.082(7)–3.224(7) Å] that are closer than the analogous Sm...C_{methyl} contacts observed in $[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ [Sm...C 3.32(1)–3.46(1) Å].²¹ The approximately planar SmNSi₂ fragments in **1** are staggered with respect to each other (twist angle of 44.42 $^{\circ}$), with the deviation from 90 $^{\circ}$ attributed to agostic Sm...C_{methylene} interactions.

Formally each nitrogen atom carries a single negative charge and the Sm^{II} ion is divalent, with an [Xe]4f⁶ configuration. The f⁶ configuration leads to a formally diamagnetic $^7\text{F}_0$ ground state, with close lying excited states that provide a non-zero magnetic moment at room temperature. Magnetic measurements on **1** give a room temperature magnetic moment of 3.62 μ_{B} that falls towards zero at low temperature (Fig. S2 and S3, ESI[†]). This is clearly incompatible with interesting low temperature magnetic behaviour. However, the structure of **1** is close to the ideal linear arrangement to stabilize the large angular momentum states of Dy^{III} and produce monstrous uniaxial magnetic anisotropy.

Such a Dy^{III} compound is challenging to make; we believe a route *via* the heteroleptic $[\text{Dy}\{\text{N}(\text{Si}^i\text{Pr}_3)_2\}_2\text{I}]$ treated with the potassium salt of a large anion might work through precipitation of a potassium iodide. Other routes can be imagined, and here we present predictions of the magnetic properties of such a complex, intending to inspire synthetic work towards the linear Dy^{III} complex, and, more ambitiously, the isoelectronic Tb^{III} analogue.

The properties of $[(^i\text{Pr}_3\text{Si})_2\text{N}-\text{Dy}-\text{N}(\text{Si}^i\text{Pr}_3)_2]^+$ **2** are predicted by CASSCF/RASSI/SINGLE_ANISO²² *ab initio* calculations (see ESI[†] for details) employing the structure of **1**, where Sm^{II} has been replaced by Dy^{III}. The validity of the method was tested by calculating the variable temperature magnetic behavior of **1**, where the agreement



Fig. 3 Electronic states and magnetic transition probabilities for the ground $^6\text{H}_{15/2}$ 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 $| -15/2 \rangle$ 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).

is excellent (Fig. S2 and S3, ESI[†]). Dy^{III} has a $^6\text{H}_{15/2}$ ground multiplet, which is split by the crystal field into eight Kramer's doublets with total angular momentum projections $m_j = \pm 1/2, \pm 3/2, \dots, \pm 15/2$. The *ab initio* calculations show that the lowest six Kramer's doublets are the almost pure m_j states of $m_j = \pm 15/2, \pm 13/2, \pm 11/2, \pm 9/2, \pm 7/2$ and $\pm 5/2$, sharing a common quantization axis (Fig. 3 and Tables S1 and S2, ESI[†]). The two most energetic doublets are strongly mixed; a characteristic of low symmetry complexes due to the lack of a rigorous molecular C_{∞} axis.¹⁴ Along the main magnetic axis these two states can be expressed as $|\psi_{ab}\rangle = 64\%|\pm 3/2\rangle + 26\%|\mp 1/2\rangle$ and $|\psi_{cd}\rangle = 68\%|\pm 1/2\rangle + 31\%|\mp 3/2\rangle$ and (Table S2, ESI[†]), giving the most energetic Kramer's doublet a large g_y value of ~ 17.5 perpendicular to the main magnetic axis.

Magnetic relaxation in lanthanides follows three possible routes: (1) QTM within the ground doublet (e.g. $| -15/2 \rangle \rightarrow | +15/2 \rangle$ in Fig. 3), (2) thermally assisted QTM (TA-QTM) *via* excited states (e.g. $| -15/2 \rangle \rightarrow | -13/2 \rangle \rightarrow | +13/2 \rangle \rightarrow | +15/2 \rangle$), or (3) an Orbach process composed of direct and/or Raman mechanisms (e.g. $| -15/2 \rangle \rightarrow | -13/2 \rangle \rightarrow | +15/2 \rangle$). The most probable pathway depends on the composition of the states involved and their interactions with phonons. For example, the slow magnetic relaxation for $\{\text{Dy}_4\text{K}_2\}$ was shown to occur *via* the first or second excited states (TA-QTM), depending on the number and location of neighboring Dy^{III} ions providing a source of transverse magnetic field.⁷ The states with opposing magnetic projections are mixed proportionally to the product of the transverse field and the transverse g -factors and therefore TA-QTM will occur *via* the excited state which has transverse



