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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,  $U_{\text{eff}}$ , for reorientation of magnetization of 1800 cm<sup>-1</sup>.**

Since their initial discovery,<sup>1</sup> single molecule magnets (SMMs) have been lauded as candidates for high density data storage devices.<sup>2</sup> A major breakthrough in the field<sup>3</sup> occurred in 2003 with the observation of SMM behavior in a monometallic {TbPc<sub>2</sub>}<sup>-</sup> complex with an energy barrier,  $U_{\text{eff}} = 230 \text{ cm}^{-1}$ .<sup>4</sup> The ensuing decade saw rapid growth in lanthanide SMMs<sup>5</sup> with the  $U_{\text{eff}}$  barrier to magnetization reversal increased to 652 cm<sup>-1</sup> for another derivative of {TbPc<sub>2</sub>}<sup>-</sup>,<sup>6</sup> and 585 cm<sup>-1</sup> for a polymetallic Dy@{Y<sub>4</sub>K<sub>2</sub>} complex.<sup>7</sup> The highest blocking temperature  $T_{\text{B}}$  (*i.e.* the temperature at which hysteresis is observed) was also increased to 14 K, *via* an N<sub>2</sub><sup>3-•</sup> radical bridge in a {Tb<sub>2</sub>N<sub>2</sub><sup>3-•</sup>} complex.<sup>8</sup>

Although three of these milestones employ the Tb<sup>III</sup> ion, by far the most utilized lanthanide ion in SMMs is Dy<sup>III</sup> by virtue of its unique electronic structure.<sup>9</sup> Apart from a radical-bridged {Dy<sub>2</sub>N<sub>2</sub><sup>3-•</sup>} complex,<sup>10</sup> nearly all polymetallic Dy<sup>III</sup>-based SMMs possess negligible interactions between magnetic spin centres, and instead rely on the single ion anisotropy of Dy<sup>III</sup> (*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<sup>III</sup> SMMs so that doping a small amount of the paramagnetic ion into a diamagnetic host lattice (usually the Y<sup>III</sup> analogue) often results in an increased  $U_{\text{eff}}$ .<sup>7</sup>

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

(CASSCF) *ab initio* calculations<sup>12</sup> that are often employed to examine 4f complexes, pioneered by Chibotaru.<sup>7,13</sup> Electrostatic approaches suggest that the optimal ligand environment to exploit the oblate spheroidal electron density of Dy<sup>III</sup> is axial, where rigorously axial systems have the benefit of maintaining a single, unique quantization axis for the total angular momentum  $m_j$  states.<sup>14</sup> 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.<sup>2</sup>

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 {Dy<sub>5</sub>} and {Dy<sub>4</sub>K<sub>2</sub>} alkoxide complexes<sup>7</sup> because of the strongly axially repulsive crystal field potentials along the local *z*-direction of each Dy<sup>III</sup>. Other compounds such as [(C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>Ln]<sup>-</sup> (ref. 15) or Cloke's bis(arene) lanthanide complexes<sup>16</sup> 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.<sup>17</sup> A one coordinate lanthanide complex [DyO]<sup>+</sup> has been considered theoretically with a very large  $U_{\text{eff}}$  predicted,<sup>14</sup> 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(Si<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub> was designed, and synthesised from ClSi<sup>*i*</sup>Pr<sub>3</sub> and LiHN(Si<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>, and this was converted to the group 1 transfer agent [KN(Si<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>] with KH. Reacting two equivalents of [KN(Si<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>] with samarium(II) diiodide yields the mononuclear homoleptic bis(amide) complex, [(<sup>*i*</sup>Pr<sub>3</sub>Si)<sub>2</sub>N-Sm-N(Si<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>] **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)° in the solid state (Fig. 2, see ESI† for details); this near-linearity contrasts with the bent C-Ln-C angles of [Ln<sup>II</sup>{C(SiMe<sub>3</sub>)<sub>3</sub>}<sub>2</sub>] complexes (Ln = Sm, Yb, Eu).<sup>18-20</sup> The

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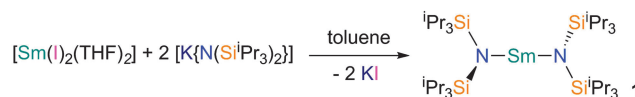
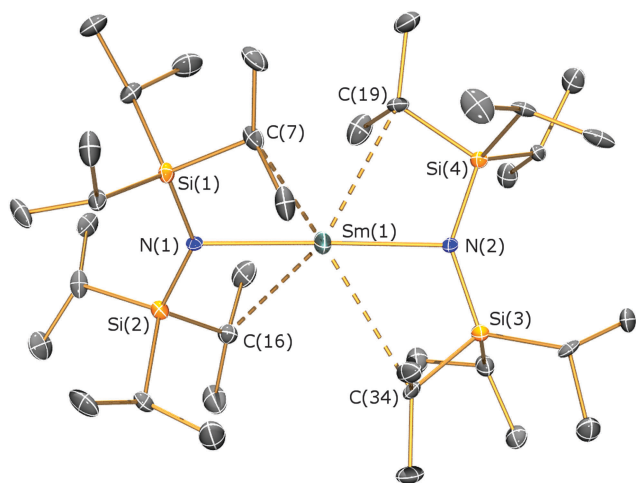


Fig. 1 Synthetic route to **1**.



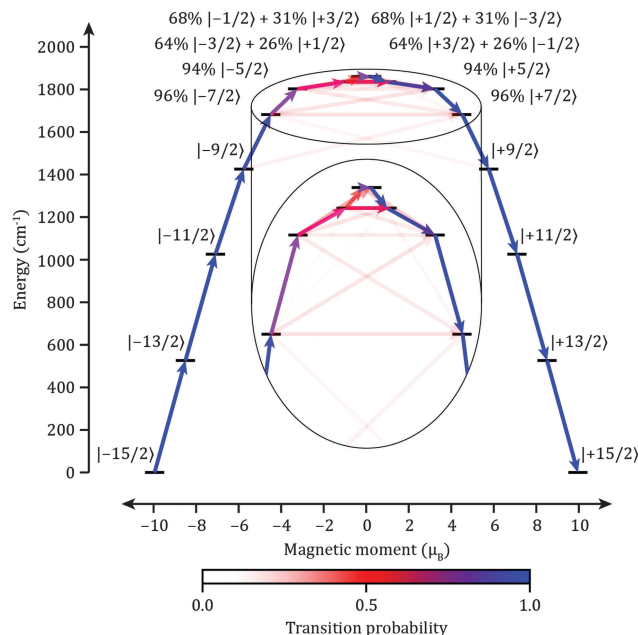


bulky <sup>i</sup>Pr groups are vital for the isolation of a homoleptic complex, as [Sm{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>](THF)<sub>2</sub>] exhibits additional O-donors.<sup>21</sup> The Sm–N distances in **1** [2.483(6) Å] are longer than those observed in [Sm{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>](THF)<sub>2</sub>] [mean Sm–N 2.433(9) Å] but this is compensated by **1** exhibiting four short Sm···C<sub>methine</sub> distances [Sm···C 3.082(7)–3.224(7) Å] that are closer than the analogous Sm···C<sub>methyl</sub> contacts observed in [Sm{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>](THF)<sub>2</sub>] [Sm···C 3.32(1)–3.46(1) Å].<sup>21</sup> The approximately planar SmNSi<sub>2</sub> fragments in **1** are staggered with respect to each other (twist angle of 44.42°), with the deviation from 90° attributed to agostic Sm···C<sub>methine</sub> interactions.

Formally each nitrogen atom carries a single negative charge and the Sm<sup>II</sup> ion is divalent, with an [Xe]4f<sup>6</sup> configuration. The f<sup>6</sup> configuration leads to a formally diamagnetic <sup>7</sup>F<sub>0</sub> 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<sub>B</sub> 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<sup>III</sup> and produce monstrous uniaxial magnetic anisotropy.

Such a Dy<sup>III</sup> compound is challenging to make; we believe a route *via* the heteroleptic [Dy{N(Si<sup>t</sup>Pr<sub>3</sub>)<sub>2</sub>}<sub>2</sub>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<sup>III</sup> complex, and, more ambitiously, the isoelectronic Tb<sup>II</sup> analogue.

The properties of  $[(\text{Pr}_3\text{Si})_2\text{N-Dy-N}(\text{Si}^i\text{Pr}_3)_2]^+$  **2** are predicted by CASSCF/RASSI/SINGLE\_ANISO<sup>22</sup> *ab initio* calculations (see ESI† for details) employing the structure of **1**, where  $\text{Sm}^{\text{II}}$  has been replaced by  $\text{Dy}^{\text{III}}$ . 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†).  $\text{Dy}^{\text{III}}$  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 Kramers 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  $C_\infty$  axis.<sup>14</sup> Along the main magnetic axis these two states can be expressed as  $|\psi_{\text{ab}}\rangle = 64\%|\pm 3/2\rangle + 26\%|\mp 1/2\rangle$  and  $|\psi_{\text{cd}}\rangle = 68\%|\pm 1/2\rangle + 31\%|\mp 3/2\rangle$  and (Table S2, ESI†), giving the most energetic Kramers doublet a large  $g_y$  value of  $\sim 17.5$  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  $\text{Dy}^{\text{III}}$  ions providing a source of transverse magnetic field.<sup>7</sup> 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

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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.*  $[(\text{Pr}_3\text{Si})_2\text{C}-\text{Dy}-\text{C}(\text{Si}^+\text{Pr}_3)_2]^-$ , 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