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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 {TbPc₂}⁻ complex with an energy barrier, U_{eff} = 230 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 {TbPc₂}⁻,⁶ and 585 cm⁻¹ for a polymetallic Dy@{Y₄K₂} 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 N₂^{3-•} radical bridge in a {Tb₂N₂^{3-•}} 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 {Dy₂N₂^{3-•}} 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 {Dy₅} and {Dy₄K₂} alkoxide complexes⁷ because of the strongly axially repulsive crystal field potentials along the local *z*-direction of each Dy^{III}. Other compounds such as [(C₈H₈)₂Ln]⁻ (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 [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 HN(Si^{*i*}Pr₃)₂ was designed, and synthesised from ClSi^{*i*}Pr₃ and LiHN(Si^{*i*}Pr₃)₂, and this was converted to the group 1 transfer agent [KN(Si^{*i*}Pr₃)₂] with KH. Reacting two equivalents of [KN(Si^{*i*}Pr₃)₂] with samarium(II) diiodide yields the mononuclear homoleptic bis(amide) complex, [(^{*i*}Pr₃Si)₂N-Sm-N(Si^{*i*}Pr₃)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)° 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(SiMe₃)₃}₂] complexes (Ln = Sm, Yb, Eu).¹⁸⁻²⁰ The

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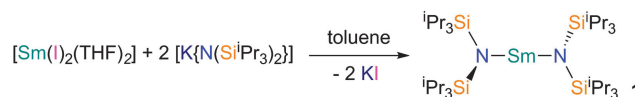


Fig. 1 Synthetic route to **1**.



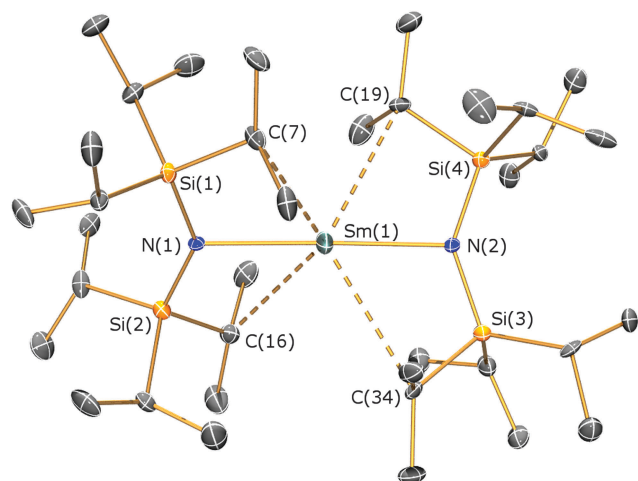


Fig. 2 Molecular structure of **1**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sm1–N1 2.483(6), Sm1–N2 2.483(6), Sm1···C7 3.180(8), Sm1···C16 3.169(8), Sm1···C19 3.082(8), Sm1···C34 3.224(8), N1–Sm1–N2 175.52(18), Sm1–N1–Si1 109.9(3), Sm1–N1–Si2 111.6(3), Si1–N1–Si2 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 [Sm{N(SiMe₃)₂}(THF)₂] exhibits additional O-donors.²¹ The Sm–N distances in **1** [2.483(6) Å] are longer than those observed in [Sm{N(SiMe₃)₂}(THF)₂] [mean Sm–N 2.433(9) Å] but this is compensated by **1** exhibiting four short Sm···C_{methine} distances [Sm···C 3.082(7)–3.224(7) Å] that are closer than the analogous Sm···C_{methyl} contacts observed in [Sm{N(SiMe₃)₂}(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°), with the deviation from 90° attributed to agostic Sm···C_{methine} 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 ⁷F₀ 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 [Dy{N(SiⁱPr₃)₂}] 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 [(ⁱPr₃Si)₂N–Dy–N(SiⁱPr₃)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

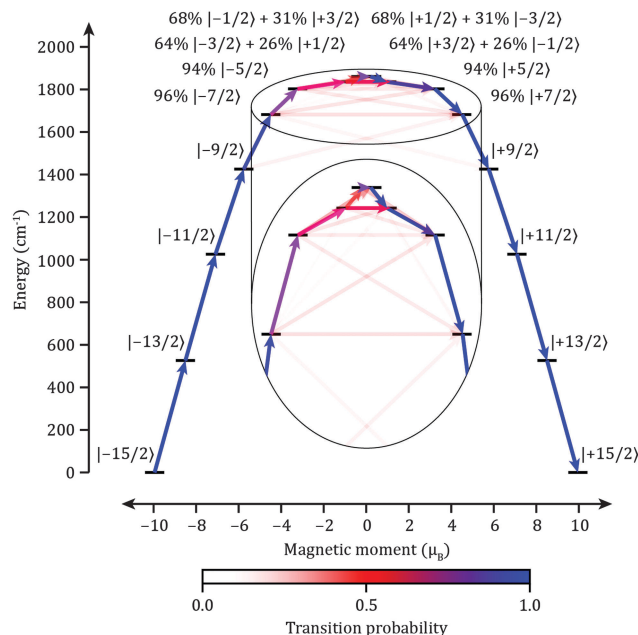


Fig. 3 Electronic states and magnetic transition probabilities for the ground ⁶H_{15/2} multiplet of **2** in zero field. The x-axis shows the magnetic moment of each state along the main magnetic axis of the molecule. Relaxation commences from the |-15/2> state and only includes pathways which reverse 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 ⁶H_{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> → |+15/2> in Fig. 3), (2) thermally assisted QTM (TA-QTM) *via* excited states (e.g. |-15/2> → |-13/2> → |+13/2> → |+15/2>), or (3) an Orbach process composed of direct and/or Raman mechanisms (e.g. |-15/2> → |-13/2> → |+15/2>). The most probable pathway depends on the composition of the states involved and their interactions with phonons. For example, the slow magnetic relaxation for {Dy₄K₂} 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



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Notes and references

- 1 R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141.
- 2 D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford University Press, 2006.
- 3 L. Sorace, C. Benelli and D. Gatteschi, *Chem. Soc. Rev.*, 2011, **40**, 3092.
- 4 N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara and Y. Kaizu, *J. Am. Chem. Soc.*, 2003, **125**, 8694.
- 5 D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield, *Chem. Rev.*, 2013, **113**, 5110.
- 6 C. R. Ganivet, B. Ballesteros, G. de la Torre, J. M. Clemente-Juan, E. Coronado and T. Torres, *Chem. – Eur. J.*, 2013, **19**, 1457.
- 7 R. J. Blagg, L. Ungur, F. Tuna, J. Speak, P. Comar, D. Collison, W. Wernsdorfer, E. J. L. McInnes, L. F. Chibotaru and R. E. P. Winpenny, *Nat. Chem.*, 2013, **5**, 673.
- 8 J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 14236.
- 9 D. Gatteschi, *Nat. Chem.*, 2011, **3**, 830.
- 10 J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *Nat. Chem.*, 2011, **3**, 538–542.
- 11 J. D. Rinehart and J. R. Long, *Chem. Sci.*, 2011, **2**, 2078.
- 12 N. F. Chilton, D. Collison, E. J. L. McInnes, R. E. P. Winpenny and A. Soncini, *Nat. Commun.*, 2013, **4**, 2551.
- 13 L. Ungur, J. J. Le Roy, I. Korobkov, M. Murugesu and L. F. Chibotaru, *Angew. Chem., Int. Ed.*, 2014, **53**, 4413.
- 14 L. Ungur and L. F. Chibotaru, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20086.
- 15 (a) F. Mares, K. Hodgson and A. Streitwieser, Jr., *J. Organomet. Chem.*, 1970, **24**, C68; (b) K. R. Meihaus and J. R. Long, *J. Am. Chem. Soc.*, 2013, **135**, 17952.
- 16 For example, J. G. Brennan, F. G. N. Cloke, A. A. Sameh and A. Zalkin, *Chem. Commun.*, 1987, 1668.
- 17 J. M. Zadrozny, D. J. Xiao, M. Atanasov, G. J. Long, F. Grandjean, F. Neese and J. R. Long, *Nat. Chem.*, 2013, **5**, 577.
- 18 C. Eaborn, P. B. Hitchcock, K. Izod and J. D. Smith, *J. Am. Chem. Soc.*, 1994, **116**, 12071.
- 19 C. Eaborn, P. B. Hitchcock, K. Izod, Z.-R. Lu and J. D. Smith, *Organometallics*, 1996, **15**, 4783.
- 20 G. Qi, Y. Nitto, A. Saiki, T. Tomohiro, Y. Nakayama and H. Yasuda, *Tetrahedron*, 2003, **59**, 10409.
- 21 W. J. Evans, D. K. Drummond, H. Zhang and J. L. Atwood, *Inorg. Chem.*, 1988, **27**, 575.
- 22 (a) G. Karlström, R. Lindh, P.-Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig and P. Neogrady, *et al.*, *Comput. Mater. Sci.*, 2003, **28**, 222; (b) V. Veryazov, P. Widmark, L. Serrano-Andrés, R. Lindh and B. O. Roos, *Int. J. Quantum Chem.*, 2004, **100**, 626; (c) F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P. Malmqvist, P. Neogrady, T. B. Pedersen, M. Pitoňák, M. Reiher and B. O. Roos, *et al.*, *J. Comput. Chem.*, 2010, **31**, 224; (d) L. F. Chibotaru and L. Ungur, *J. Chem. Phys.*, 2012, **137**, 064112.
- 23 A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Oxford University Press, 1970.
- 24 L. Ungur, M. Thewissen, J.-P. Costes, W. Wernsdorfer and L. F. Chibotaru, *Inorg. Chem.*, 2013, **52**, 6328.
- 25 R. Marx, F. Moro, M. Dörfel, L. Ungur, M. Waters, S. D. Jiang, M. Orlita, J. Taylor, W. Frey, L. F. Chibotaru and J. van Slageren, *Chem. Sci.*, 2014, **5**, 3287.
- 26 E. Moreno Pineda, N. F. Chilton, R. Marx, M. Dörfel, D. O. Sells, P. Neugebauer, S.-D. Jiang, D. Collison, J. van Slageren, E. J. L. McInnes and R. E. P. Winpenny, *Nat. Commun.*, 2014, **5**, 6243.
- 27 F. Moro, D. P. Mills, S. T. Liddle and J. van Slageren, *Angew. Chem., Int. Ed.*, 2013, **52**, 3430.
- 28 R. A. Layfield, *Organometallics*, 2014, **33**, 1084.

While 2 would have a huge U_{eff} , an even higher U_{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_{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