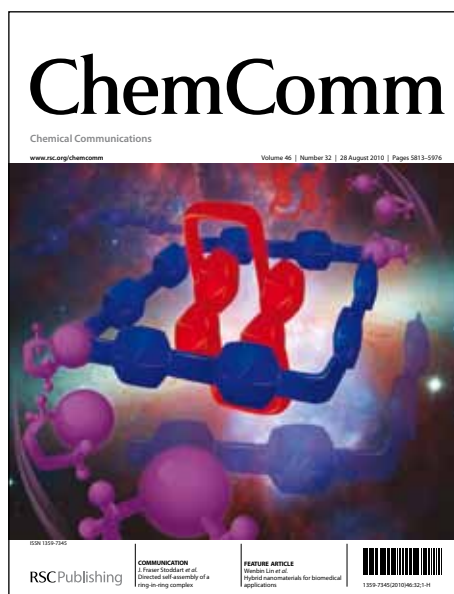


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COMMUNICATION

Sandwich Complex with Axial Symmetry for Harnessing the Anisotropy in a Prolate Erbium(III) Ion.

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A mononuclear Er^{III} sandwich type complex, [Li(DME)₃][Er^{III}(COT²⁻)₂], was isolated using 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (COT²⁻). Remarkably, this low-symmetry complex exhibits magnet-like behavior of magnetic remanence and coercivity in the hysteresis loops up to 8K with an energy barrier (U_{eff}) of 187(1) K, thus making this molecule a unique Single-Ion Magnet.

Since the discovery of magnet-like behavior in the form of slow relaxation of the magnetization in a discrete molecule (Mn₁₂Ac) in the early 90's, several hundreds of transition metal complexes have been reported displaying similar behaviour.¹ Such molecules are termed Single-Molecule Magnets (SMMs) and hold tremendous application potential in high-density data storage and/or quantum computation due to their magnetic moment bistability. In order to have application potential in memory storage devices it is imperative that SMMs have high blocking temperatures, i.e. the temperature below which magnet-like behavior is observed. Although transition metal SMMs are prevalent, their blocking temperatures remain below 5 K. However, since 2003² the emergence of lanthanide based nanomagnets have led to much higher energy barriers³ and blocking temperatures.^{3a,4}

Significant intrinsic spin-orbit coupling, in addition to the large number of unpaired electrons in lanthanide ions, make them ideal candidates for attaining large spin-reversal barriers. As such, even mononuclear lanthanide complexes exhibit SMM behaviour. These monometallic SMMs or so called Single-Ion Magnets (SIMs) are ideally suited as Qubits,⁵ i.e. the quantum analogue of the classical bit, as they can exhibit superposition of two quantum mechanical states. Moreover, they represent the smallest nanomagnets and thus have the largest high-density storage potential. Therefore, several SIMs are reported with late lanthanide ions of which Dy^{III} is the most prolific. Crystal field environment is important for such systems, as coordination

environment, local symmetry and ligand donation can each influence the overall anisotropy of the system and subsequently the energy barrier.⁶ With the aim of attaining high blocking temperature SIMs, we have recently focused our attention on organometallic sandwich complexes using substituted planar COT ligands.⁷ This methodology uses a delocalized π cloud to promote crystal field influence on the lanthanide ion's ground state and subsequently influence the direction of the anisotropic axis (which will dictate the overall magnetic behavior). In fact, it is necessary to obtain strong axial anisotropy to achieve blocking of the magnetization at high temperatures, and the use of planar COT ligands is ideal for attaining compounds with high axial symmetry.

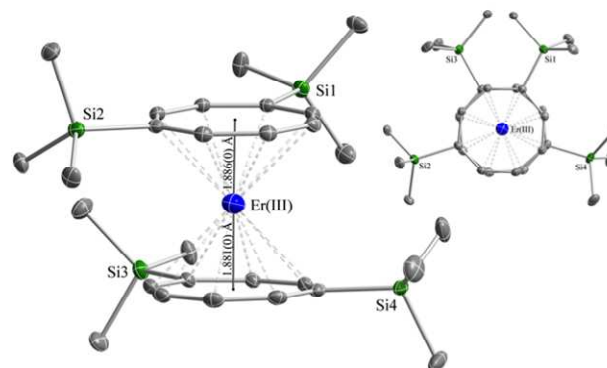


Figure 1. Molecular X-ray structure of [Er^{III}(COT²⁻)₂]. Hydrogen atoms and Li(DME)₃ counter ion are omitted for clarity. Top view (right) illustrates staggered arrangement of C atoms in upper and lower COT²⁻ rings. Colour code: blue (Er^{III}), green (Si), grey (C). Thermal ellipsoids are shown at 30% probability.

It was recently reported that ligand electron density placed above and below the xy plane (ie. Sandwich complexes) is best for maximizing the anisotropy of oblate ions such as Dy^{III} ions.⁸ Whereas if the same ligand environment was applied to a prolate ion, such as Er^{III}, electron repulsion between the ligand and metal can lead to reduced anisotropic barriers.⁷ In contrast, based on our synthetic development, we recently reported^{7b} *ab-initio* calculations suggesting that the replacement of Dy^{III} with Er^{III} in COT sandwich-complexes will likely enhance SIM behaviour. Therefore, in order to further understand the isostructural crystal field effects on different lanthanide ions, we have created an Er^{III} analogue to our previously reported Dy^{III} complex.^{7b} Herein, we

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† Electronic Supplementary Information (ESI) available: Details of crystallographic information of [Li(DME)₃][Er^{III}(COT²⁻)₂], experimental details, IR, NMR, SQUID magnetic measurements and supplementary figures. CCDC 863401. See DOI: 10.1039/b000000x/

present an Er^{III} SIM based on planar 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (COT²⁻) exhibiting magnetic hysteresis at 8K.

The preparation of sandwich-type complexes using substituted 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (COT²⁻) was initially reported by Edelman, we have since prepared mono and dinuclear Dy^{III} as well as Gd^{III} complexes.⁷ The mononuclear Er^{III} analog, [Li(DME)₃][Er^{III}(COT²⁻)₂], (**1**), was synthesized using the same synthetic conditions employed for the isolation of the Dy^{III} analogue.^{7b} Single crystal X-ray analysis revealed that **1** crystallizes in an triclinic *P*-1 space group. The structure is composed of two dianionic COT²⁻ ligands bound in η⁸ fashion to the central Er^{III} ion (Fig. 1, S1), and a counter cation composed of 1 equivalent of [Li(DME)₃]. The average Er^{III}-COT²⁻ distance of 1.264 Å for **1** is slightly shorter than the 2.66 Å seen in the Dy^{III} analogue^{7b} which is consistent with lanthanide contraction. The near identical Er^{III}-COT²⁻ centroid distances (1.8858(0.0015) vs. 1.8806(0.0015)Å) indicate equivalent ligand donation for both COT²⁻ rings. Minor deviation is due to short contact with the counter ion in the lattice. The near linear structure is reflected in the COT²⁻ centroid-Er^{III}-COT²⁻ centroid angle (176.45(0.05)°) which deviates from perfect linearity by 3.55°.

In order to understand the consequence of this ligand architecture on the local anisotropy of the Er^{III} ion, magnetic susceptibility measurements were performed using a SQUID magnetometer on freshly prepared ground polycrystalline samples of **1** sealed under N₂ to prevent sample degradation. Direct current (dc) magnetic susceptibility measurements were conducted in the temperature range of 1.8-300 K under a 0.1 T applied dc field (Fig. S2). The room temperature χT value of 11.35 cm³K·mol⁻¹ is in good agreement with the theoretical value of 11.48 cm³K·mol⁻¹ for a mononuclear Er^{III} (⁴I_{15/2}, S=3/2, L=6, g_J=6/5) complex. Upon decrease of the temperature, the χT product remains nearly constant then decreases gradually between 50 and 10 K. Below 10 K there is a drastic decrease reaching a minimum value of 2.32 cm³K·mol⁻¹ at 1.8 K, this behavior is attributed to significant anisotropy as seen in some highly anisotropic complexes.^{4a,c,9} Field dependent magnetization measurements (*M* vs. *H*) reveal a rapid and steady increase of the magnetization at 8 K without clear saturation at 7 T (Fig. S3). At temperatures below 5 K there is a sinusoidal character observed at applied field under 1T. Such a signature feature can be due to quantum tunneling of the magnetization (QTM) or intermolecular interactions. In **1** metal centers are separated by at least 10.39 Å, thus, intermolecular interactions are negligible. The non-saturation as well as the non-superimposition of iso-temperature lines in the *M* vs. *H*/*T* data also confirms the presence of significant magnetic anisotropy in **1** (Fig. S3).

To further investigate blocking of the magnetization, temperature dependent hysteresis measurements were carried out between -5 to 5 T and 1.8 to 10 K (Fig. 2). At a fixed sweep rate of 22 Oe·S⁻¹ and at 1.8 K the appearance of a clear hysteresis with coercivity is observed. Remarkably, at *M*=0 a large coercive field of ~6250 Oe can be seen at 1.8K (Fig. S4). Upon increase of the temperature, coercivity decreases and closes at *M*=0 around 8K. Above 8K, phonon bottleneck-type hysteresis with small openings can be seen which disappear above 9K. Such a large blocking temperature and coercive field have never before been

reported for a Single-Ion Magnet. Moreover, at *H*=0 remnant magnetization can be seen which is unique for a SIM. It is noteworthy that the step-like feature at ±4500 Oe is most likely arising from thermally assisted QTM behavior while the step at zero field is due to ground state tunneling. Although ground state QTM is expected to be suppressed for a Kramer system, environmental degrees of freedom as well as hyperfine and dipolar coupling *via* transverse field components can result in non-negligible QTM.¹⁰ Additionally, QTM can be minimized in complexes with high symmetry around the metal center,¹¹ however, the presence of trimethylsilyl groups in **1** low to low molecular symmetry of the molecule, therefore, removal of such groups may yield an even larger coercive field. This further confirms the intricacies of secondary coordination environments on local anisotropy of a lanthanide molecule.^{10, 7b} Further single crystal studies are required to confirm potential fine structures in the hysteresis as well as tunnel-crossing levels.

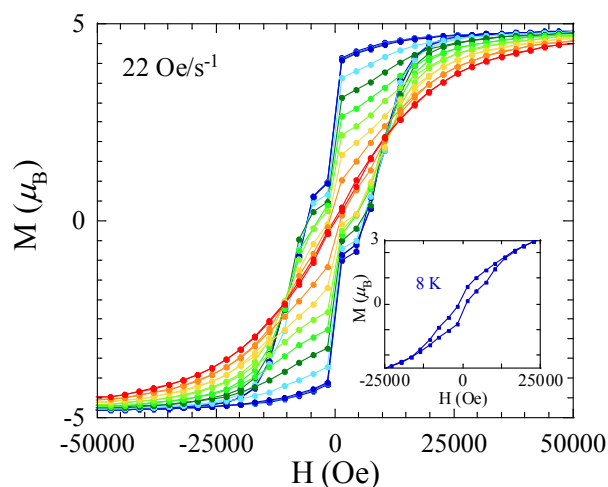


Figure 2. Magnetic hysteresis data for **1** between 1.8-10 K. Data was collected at an average sweep rate of 22 Oe·s⁻¹. In all measurements data was collected starting at *H*=0 Oe, sweeping to *H*=50 kOe and then cycling to *H*=-50 kOe and back to *H*=50 kOe. Solid lines are guides for the eye. In complex **1**, coercivity is observed up to 8 K (insert) at *M*=0.

Ac susceptibility measurements were performed to gain insight into the dynamics of magnetization relaxation, using an oscillating field of 3 Oe. Below 31 K a frequency dependent in-phase (χ') (Fig. S5) and out-of-phase (χ'') (Fig. 3) component of the ac signal was observed indicating slow relaxation of magnetization, thus confirming SIM behavior.

Using the maximum out-of-phase susceptibility (χ'') between 11-25 K (Fig. 3) and the Arrhenius law, an effective energy barrier of 187(1) K with a τ₀=4.0×10⁻⁸s (Fig. S6) was obtained. A blocking temperature of 8 K can be obtained at 100s from extrapolation of the Arrhenius data, which is consistent with hysteresis measurements. It is noteworthy that this energy barrier is significantly larger than the 25 K obtained for the Dy^{III} analogue.^{7b} Moreover, there is only one clear relaxation process apparent, in contrast to the Dy^{III} analogue where multiple relaxations were observed.^{7b} Competing relaxation mechanisms are likely the cause of the small energy barrier observed in the Dy^{III} analog. Likewise the graphical representation of χ'' vs. χ' (Cole-Cole plot, Fig. 4) between 11 – 24 K undoubtedly confirms

the single relaxation process occurring in **1**. This data was fitted using a generalized Debye model which led to small α parameter with a narrow distribution (0.010 to 0.080).

The magnetic comparison between **1** and the Dy^{III} analogue directly contradicts the speculation that a sandwich-type ligand field is more favourable to yield stronger SIM behaviour in oblate Ln^{III} ions. Arguably the TMS groups on the COT²⁻ ligand can also have a large effect on the direction of the main anisotropy axis.^{7b} However, removal of the TMS groups will likely only enhance SIM behaviour as predicted by our previously reported *ab initio* calculations^{7b}

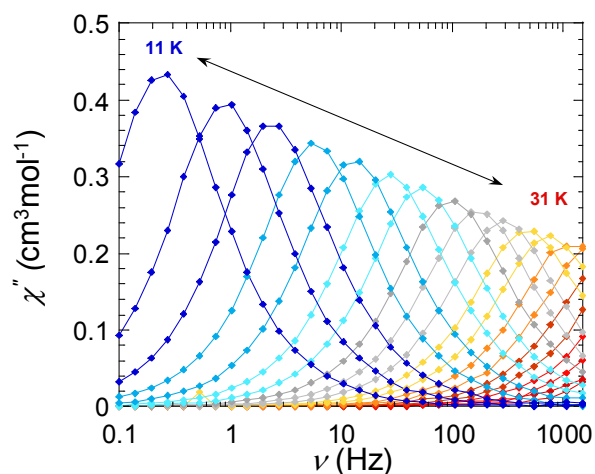


Figure 3. Out-of-phase susceptibility (χ'') versus frequency (ν) for **1** in the temperature range 11–31 K at 0 dc field.

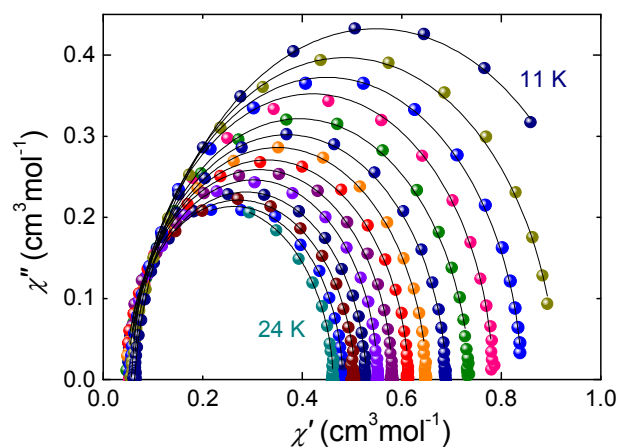


Figure 4. Cole-Cole plot for ac susceptibility of **1** collected between 11–24 K. Experimental data points are represented by circles and the solid black line represents a fit to the data. Small α^2 values with a narrow distribution (0.010 to 0.080) confirm the magnetic susceptibility of **1** is unique to a single relaxation process.

A homoleptic [Er^{III}(COT²⁻)₂] SIM was reported to have one of the highest blocking temperatures of any SMM. In comparison with [Cp*Er(COT)]^{9b} the better performance of **1** most likely arises from more equivalent ligand donation above and below the *xy* plane, and thus higher axial orientation of the anisotropy axis. Results also suggest that the significant enhancement in the energy barrier against spin reversal of **1** in comparison to the

Dy^{III} analog can also be attributed to the orientation of the anisotropy axis. This comparison highlights that although isostructural compounds can be obtained in late lanthanide chemistry, the electron count and inherent magnetic anisotropy of each individual metal ion leads to unique behavior. This small SIM with magnet-like behavior clearly suggests that if such inherent anisotropy can be harnessed in single ions, better performing SMMs are achievable. The observed features of remanence and coercivity are signature characteristics of permanent magnets, thus, the remarkable performance of this SIM makes it viable for application in high-density data storage.

We thank the University of Ottawa, the Canada Foundation for Innovation (CFI), NSERC (Discovery and RTI grants) for financial support. We also thank Dr. L. Ungur and Prof. L. F. Chibotaru for insightful discussions.

Notes and references

- (a) R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature* 1993, **365**, 141. (b) H. Zhao, C. P. Berlinguette, J. Bacsá, A. V. Prosvirin, J. K. Bera, S. E. Tichy, E. J. Schelter and K. R. Dunbar, *Inorg. Chem.* 2004, **43**, 1359. (c) D. J. Price, S. R. Batten, B. Moubaraki and K. S. Murray, *Chem. Commun.* 2002, 762.
- N. Ishikawa, M. Sugita, T. Ishikawa, S.-y. Koshihara and Y. Kaizu, *J. Am. Chem. Soc.* 2003, **125**, 8694.
- (a) M. Gonidec, R. Biagi, V. Corradini, F. Moro, V. De Renzi, U. del Pennino, D. Summa, L. Muccioli, C. Zannoni, D. B. Amabilino and J. Veciana, *J. Am. Chem. Soc.* 2011, **133**, 6603. (b) 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. (c) M. Gonidec, F. Luis, A. Vilchez, J. Esquena, D. B. Amabilino and J. Veciana, *Angew. Chem. Int. Ed.* 2010, **49**, 1623.
- (a) J. D. Rinehart, M. Fang, W. J. Evans and R. J. Long, *J. Am. Chem. Soc.* 2011, **133**, 14236. (b) P.-H. Lin, T. J. Burchell, L. Unger, L. F. Chibotaru, W. Wernsdorfer and M. Murugesu, *Angew. Chem., Int. Ed.* 2009, **48**, 9489. (c) J. D. Rinehart, M. Fang, W. J. Evans and J. Long, *Nat. Chem.* 2011, **3**, 538.
- (a) J. J. Baldov, S. Cardona-Serra, J. M. Clemente-Juan, E. Coronado, A. Gaita-Arín and A. Pali, *Inorg. Chem.* 2012, **51**, 12565. (b) M. D. Jenkins, T. Hümmel, M. J. Martínez-Pérez, J. García-Ripoll, D. Zueco and F. Luis, *New J. Phys.* 2013, **15**, 095007. (c) G. A. Timco, S. Carretta, F. Troiani, F. Tuna, R. J. Pritchard, C. A. Muryn, E. J. L. McInnes, A. Ghirr, A. Candini, P. Santini, G. Amoretti, M. Affronte and R. E. P. Winpenny, *Nat. Nanotech.* 2009, **4**, 173. (d) D. N. Woodruff, R. E. P. Winpenny, R. A. Layfield *Chem. Rev.*, 2013, **113**, 5110.
- (a) T. Glaser, M. Heidemeier, T. Weyhermüller, R.-D. Hoffmann, H. Rupp and P. Müller, *Angew. Chem. Int. Ed.* 2006, **45**, 6033. (b) D.-P. Li, T.-W. Wang, C.-H. Li, D.-S. Lin, Y.-Z. Li and X.-Z. You, *Chem. Commun.* 2010, **46**, 2929. (c) M. A. Aldamen, J. M. Clemente-Juan, E. Coronado, C. Martí-Gastaldo and A. Gaita-Arino, *J. Am. Chem. Soc.* 2008, **130**, 8874.
- (a) M. Jeletic, P.-H. Lin, J. J. Le Roy, I. Korobkov, S. I. Gorelsky and M. Murugesu, *J. Am. Chem. Soc.* 2011, **133**, 19286. (b) J. J. Le Roy, M. Jeletic, S. I. Gorelsky, I. Korobkov, L. Ungur, L. F. Chibotaru and M. Murugesu, *J. Am. Chem. Soc.* 2013, **135**, 3502.
- J. D. Rinehart and J. R. Long, *Chem. Sci.* 2011, **2**, 2078.
- (a) J. M. Zadrozny, D. J. Xiao, M. Atanasov, G. J. Long, F. Grandjean, F. Neese and J. R. Long, *Nat. Chem.* 2013, **5**, 577. (b) S.-D. Jiang, B.-W. Wang, H.-L. Sun, Z.-M. Wang and S. Gao, *J. Am. Chem. Soc.* 2011, **133**, 4730.
- F. Habib, P.-H. Lin, J. Long, I. Korobkov, W. Wernsdorfer and M. Murugesu, *J. Am. Chem. Soc.* 2011, **133**, 8830.
- G. Cucinotta, M. Perfetti, J. Luzon, M. Etienne, P.-E. Car, A. Caneschi, G. Calvez, K. Bernot and R. Sessoli, *Angew. Chem. Int. Ed.* 2012, **51**, 1606.