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

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Supplemental Information

Contents

1 General synthetic consideration

All manipulations were performed under an inert atmosphere using standard Schlenk or glove box techniques. Glassware was oven dried (120ºC, 6h) before use. Hexanes and dimethoxyethane (DME) were dried using activated alumina and stored over 3Å molecular sieves. Anhydrous $ErCl_3$ was purchased from Strem and used as received. All other reagents were purchased from Thermo Fisher Scientific and used without further purification. $[Li_4(COT'')_2(THF)_4]$ was synthesized using a previously published procedure.[1] ^{1}H spectra were recorded on a 300 MHz Bruker Advance instrument at room-temperature (21-23°C). Chloroform-d was degassed using repeated freezing-evacuating-thawing cycles, and stored over 4Å molecular sieves. IR data were collected on a Varian 640 FT-IR spectrometer.

1.1 Synthesis of $[Li(DME)_3][Er^{III}(COT'')_2]$ (1)

To a 20 mL scintillation vial $ErCl_3$ (0.045 g, 0.164 mmol) and $[Li4(COT'')_2(THF)_4]$ (0.197 g, 0.246 mmol) were added. The reagents were stirred in 7 mL of DME at room temperature for 36 h. After 36 h 2 mL of hexanes was added to the solution while stirring and the precipitate (LiCl) was immediately filtered off through a fine fritted funnel containing Celite®. Large orange block crystals suitable for x-ray diffraction were grown from a concentrated solution (1:1 DME:hexanes) providing $[Li(DME)_3][Er^{III}(COT'')_2]$, in 67% yield, 103 mg. Isolated crystals are air and moisture sensitive. Selected IR data for **1** (cm^{-1}): 3028 (w), 2950 (br), 2892 (m), 1447 (w), 1243 (s), 1080 (w), 1051 (s), 980 (w), 934 (m), 909 (w), 831 (s), 747 (m), 728 (m), 680 (w), 635 (w). ^{1}H NMR (300 MHz, $CDCl_3$) of $[Li(DME)_3][Er^{III}(COT'')_2]$; δ7.2 (br), δ 4.7 (br), δ 4.3 (br), 1.1 (br), δ 0.7 (br), δ -0.1 (br).

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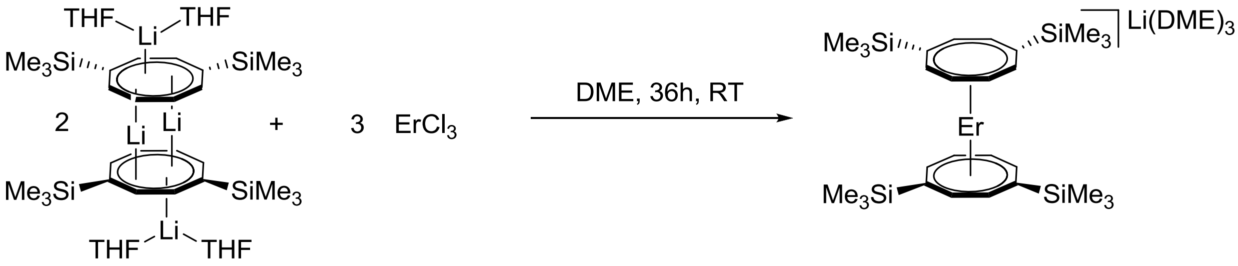
[1] M. Jeletic, F. Perras, S. Gorelsky, J. J. Le Roy, I. Korobkov, D. Bryce and M. Murugesu, *Dalton Trans*. 2012, **41**, 8060.



Scheme S1. Synthetic route to **1**, solid state complex is isolated in 50% v/v DME/hexanes.

2 X-ray crystallographic details

A suitable prism shaped crystal of **1** was mounted in inert oil and transferred to the cold gas stream of the diffractometer. Unit cell measurements and intensity data were collected at 200 K on a Bruker-AXS SMART 1 k CCD diffractometer using graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS).[2] The crystal structure was solved and refined using the SHELXTL[3] program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 863401.

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[2] Sheldrick, G. M. SADABS — Bruker AXS area detector scaling and absorption, version 2008/1, University of Göttingen, Germany, **2008**.

[3] G. M. Sheldrick, *Acta Cryst*. 2008, **A64**, 112.

2.1 Solid state structure of 1

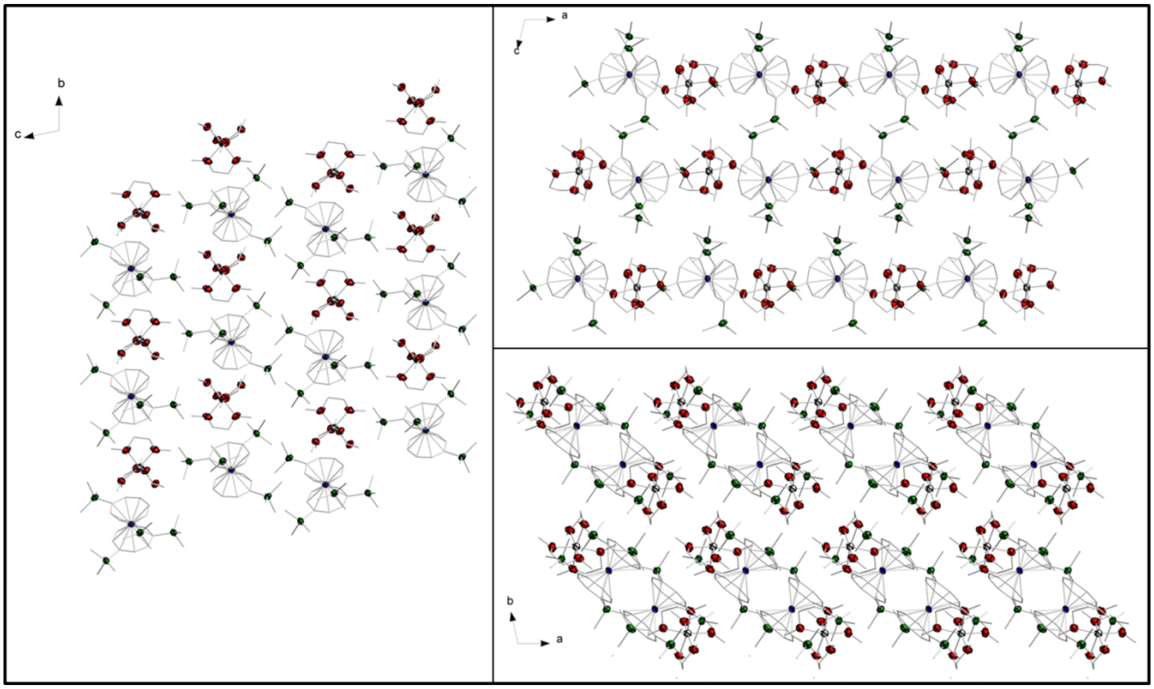

Figure S1. Packing arrangement of **1** looking down the *a* (left) *b* (top right) and *c* (bottom right) axis. H atoms are omitted for clarity. Color code: Si = green, Er = blue, Li = yellow, O = red, C = grey.

2.2 Structure refinement details

Table S1: Crystal data and structure refinement for **1**.

	1
Formula	$C_{40}H_{78}ErLiO_6Si_4$
M$_r$ (g/mol)	941.58
Crystal system	Triclinic
Space group	P-1
a **(Å)**	11.4921(12)
b **(Å)**	12.3172(12)
c **(Å)**	18.5804(19)
α (deg)	99.322(2)
β (deg)	102.182(2)
γ (deg)	100.000(2)
V (Å^3)	2477.3(4)
T(K)	200(2)
Z	2
Reflections collected	23950
goodness of fit	1.019
Shape and Color	Block orange
ρ_{calc} (cm^{-3})	1.262
R1/ wR2	0.0177 /0.0473
Size (mm)	0.12 x 0.12 x 0.12
Reflections with *I* >2σ(*I*)	11522

3 Superconducting quantum interference device (SQUID) measurements

Magnetic susceptibility measurements for **1** was obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K for dc applied fields ranging from -7 to 7 T. Dc analyses was performed on a crushed polycrystalline sample in grease, sealed in a polyethylene membrane (prepared in an inert atmosphere) under a field ranging from 0 to 7 T and temperatures between 1.8 and 300 K. Ac susceptibility measurements were carried out under an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz and dc fields ranging from 0 to 1600 Oe. Diamagnetic corrections were applied for the sample holder and the core diamagnetism from the sample (estimated with Pascal constants).

3.1 Dc magnetic susceptibility

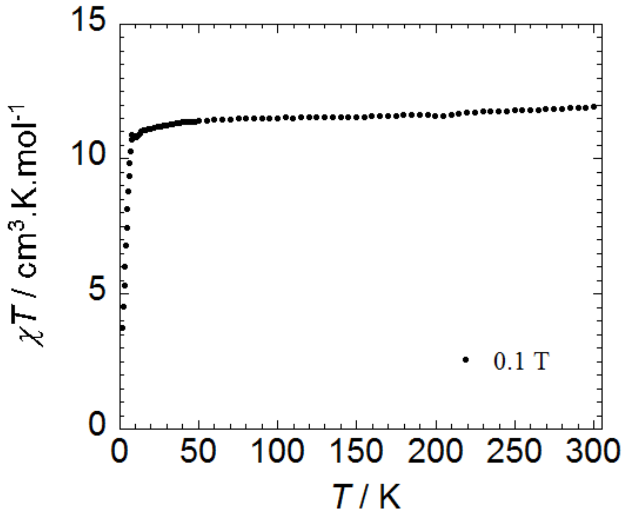

Figure S2. Temperature dependence of the χT product under 0.1 T for complex **1** with χ being the molar susceptibility per complex defined as M/H.

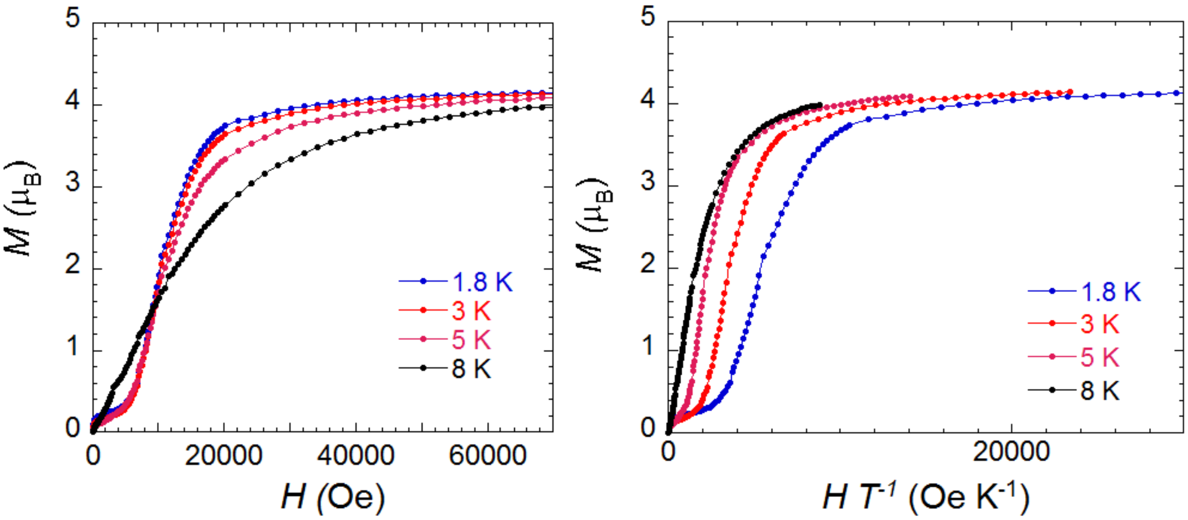

Figure S3. Field dependence of the magnetization (left) and reduced magnetization (right) for **1** at the indicated temperatures.

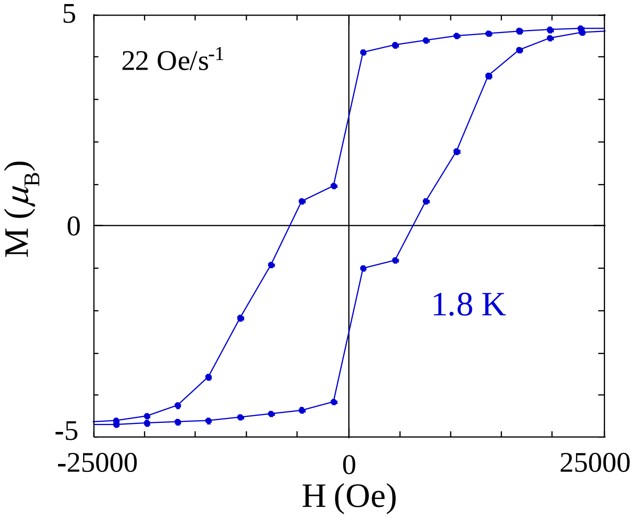

Figure S4. Magnetic hysteresis data for **1** at 1.8 K. Data was collected at an average sweep rate of 22 Oe.s^{-1}. Data was collected starting at H=0 Oe, sweeping to H=50 kOe and then cycling to H= -50 kOe and back to H=50 kOe. Solid line is a guide for the eye.

3.2 Ac magnetic susceptibility

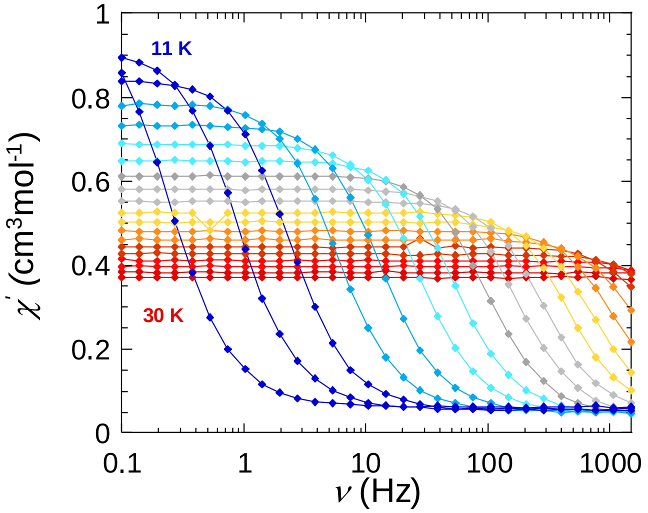

Figure S5. Variable temperature in-phase (χ') magnetic susceptibility of **1** under 0 Oe dc field and the indicated temperature range.

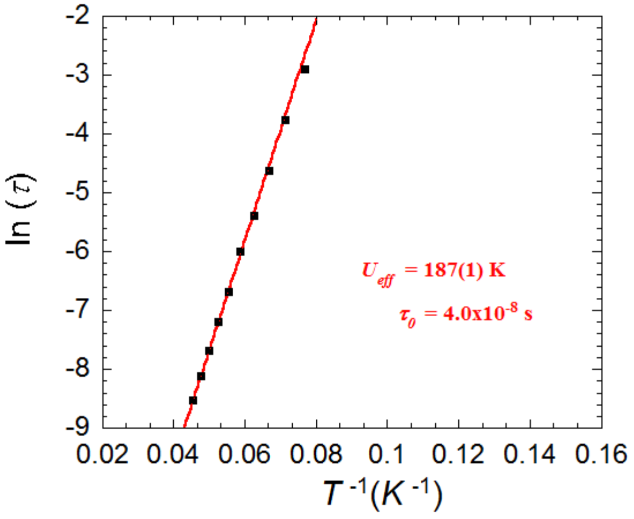

Figure S6. Relaxation time of the magnetization ln(τ) *vs*. T^{-1} for **1** (Arrhenius plot using ac data) under 0 Oe applied dc field. The solid line corresponds to the fit.