Chemical Communications

Supplementary Information for:

Single-molecule magnetism in cyclopentadienyl-dysprosium chlorides

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General experimental considerations

All synthetic manipulations were performed using standard Schlenk techniques. Toluene was degassed and dried by refluxing over sodium-potassium alloy under nitrogen.

X-ray diffraction data on 1a, 1b and 2 were collected on an OXFORD Diffraction XCaliber2 CCD diffractometer using MoKα radiation.

SQUID measurements were carried out on polycrystalline samples of 1 and 2 by enclosing the sample in O-ring-sealed Kel-F capsules. The capsules were transferred to sample holders in a glovebox, transported to the SQUID magnetometer in a sealed Schlenk tube, and then rapidly transferred to the helium-purged sample space of the magnetometer. Corrections for diamagnetism were made using Pascal’s constants.

Synthesis of 1a and 1b. A freshly prepared solution of sodium cyclopentadienide (37 mmol) in thf (60 mL) was added to a stirred suspension of anhydrous dysprosium(III) chloride (5.00 g, 18 mmol) in thf (100 mL) at 0°C. The mixture was refluxed for 16 hours and the solvent then evaporated under reduced pressure, producing a pale yellow solid. Sublimation of the yellow solid (10⁻³ mbar/180°C) resulted in the formation of yellow single-crystals of \([\text{Cp}_2\text{Dy(μ-Cl)}]_2\) (1a) and \([\text{Cp}_2\text{Dy(μ-Cl)}]_\infty\) (1b), suitable for X-ray diffraction. Total yield of \([\text{Cp}_2\text{Dy(μ-Cl)}]_n\) (3.27 g, 54%). Elemental analysis calculated (%) for C₁₀H₁₀ClDy: C 36.60, H 3.07; found C 37.12, H 2.99.

Synthesis of 2. A mixed polymorph sample of 1a/1b (1.50 g, 2 mmol) was transferred to a Soxhlet apparatus and repeatedly extracted with hot thf for 6 hours. Slow cooling of the resulting yellow solution produced large yellow crystals of \([\text{Cp}_2\text{Dy(thf)(μ-Cl)}]_2\) (2) (1.27 g, 70%). Elemental analysis calculated (%) for C₁₄H₁₈OClDy: C 42.01, H 4.53; found C 41.93, H 4.40.
<table>
<thead>
<tr>
<th>Crystal Data and Structure Refinement for [Cp₂Dy(μ-Cl)]₂ (1a)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
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<tr>
<td><strong>Formula weight</strong></td>
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<tr>
<td><strong>Temperature</strong></td>
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<td><strong>Wavelength</strong></td>
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<td><strong>Crystal system</strong></td>
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<td><strong>Space group</strong></td>
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<td><strong>Unit cell dimensions</strong></td>
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<tr>
<td><strong>a</strong></td>
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<tr>
<td><strong>b</strong></td>
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<tr>
<td><strong>c</strong></td>
</tr>
<tr>
<td><strong>Volume</strong></td>
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<td><strong>Z</strong></td>
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<td><strong>Density (calculated)</strong></td>
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<tr>
<td><strong>Absorption coefficient</strong></td>
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<tr>
<td><strong>F(000)</strong></td>
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<tr>
<td><strong>Crystal size</strong></td>
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<tr>
<td><strong>Theta range for data collection</strong></td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
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<tr>
<td><strong>Reflections collected</strong></td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
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<tr>
<td><strong>Completeness to theta = 28.53°</strong></td>
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<tr>
<td><strong>Absorption correction</strong></td>
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<tr>
<td><strong>Refinement method</strong></td>
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<tr>
<td><strong>Data / restraints / parameters</strong></td>
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<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
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<tr>
<td><strong>Final R indices [I&gt;2sigma(I)]</strong></td>
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<tr>
<td><strong>R indices (all data)</strong></td>
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<tr>
<td><strong>Largest diff. peak and hole</strong></td>
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<tr>
<td>Property</td>
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<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Empirical formula</td>
</tr>
<tr>
<td>Formula weight</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Wavelength</td>
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<tr>
<td>Crystal system</td>
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<td>Space group</td>
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<tr>
<td>Unit cell dimensions</td>
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<td>β</td>
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<td>c</td>
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<tr>
<td>γ</td>
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<tr>
<td>Volume</td>
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<tr>
<td>Z</td>
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<tr>
<td>Density (calculated)</td>
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<tr>
<td>Absorption coefficient</td>
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<tr>
<td>F(000)</td>
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<tr>
<td>Crystal size</td>
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<tr>
<td>Theta range for data collection</td>
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<tr>
<td>Index ranges</td>
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<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<td>Completeness to theta = 28.55°</td>
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<tr>
<td>Absorption correction</td>
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<tr>
<td>Refinement method</td>
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<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
</tr>
<tr>
<td>R indices (all data)</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
</tr>
</tbody>
</table>
Table S3. Crystal data and structure refinement for \([\text{Cp}_2\text{Dy(thf)(\(\mu\)-Cl)}]_2\) (2)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>(\text{C}<em>{28}\text{H}</em>{36}\text{Cl}_2\text{Dy}_2\text{O}_2)</td>
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<tr>
<td>Formula weight</td>
<td>800.47</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(P2_1/c)</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a = 7.9778(7) \text{ Å}, \alpha = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td>(b = 21.270(3) \text{ Å}, \beta = 108.500(11)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(c = 8.3900(9) \text{ Å}, \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Volume</td>
<td>1350.1(2) Å</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.969 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>5.713 mm(^{-1})</td>
</tr>
<tr>
<td>(F(000))</td>
<td>772</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.1 × 0.1 × 0.05 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.20 to 27.50°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>(-10 \leq h \leq 10, -24 \leq k \leq 27, -10 \leq l \leq 4)</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>5221</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2965 ([R(\text{int}) = 0.0511])</td>
</tr>
<tr>
<td>Completeness to theta = 27.50°</td>
<td>99.9 %</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<td>Max. and min. transmission</td>
<td>0.732 and 0.570</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>2965 / 90 / 152</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.132</td>
</tr>
<tr>
<td>Final (R) indices ([I&gt;2\sigma(I)])</td>
<td>(R1 = 0.0581, wR2 = 0.1139)</td>
</tr>
<tr>
<td>(R) indices (all data)</td>
<td>(R1 = 0.0907, wR2 = 0.1214)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>3.620 and -1.720 e.Å(^{-3})</td>
</tr>
</tbody>
</table>
Fig. S1. Powder X-ray diffraction pattern of a mixed polymorph sample of 1a/1b.

Fig. S2. Powder patterns of 1a (left) and 1b (right) calculated based on single-crystal diffraction data using the Mercury software. 1a has a large single peak at 6.3°, and 1b has large peaks at 5.4 and 7.6°.

Isolated 2θ peaks are present in each compound that show little overlap, allowing the determination of a mixing ratio. The experimental powder patterns shows significant peaks at 6.3° and one at 7.3°, although no peak was observed at 5.4° due to the beam stop obscuring the diffraction. Matching the intensities of the 6.3 and 7.3° peaks in the experimental powder pattern with the calculated intensities for the 6.3 and 7.6° peaks yielded an approximate mixing ratio of 3:1 for 1a:1b.
**Fig. S3.** Plots of $\chi T$ vs. $T$ for (left) 1 at $H = 0.1$ and 5 kG, and (right) 2 at $H = 1$ kG. Inset: Plots of $M$ vs. $H$ for (left) 1 and (right) 2, at temperatures between 1.8 and 15 K.

**Fig. S4.** Temperature dependence of the (left) in-phase ($\chi'$) and (right) out-of-phase ($\chi''$) ac susceptibility of 2 at zero-d.c. field and 1.55 G a.c. field oscillating at the indicated frequencies.

**Fig. S5.** Left: Frequency dependence (in zero-d.c. field) of the in-phase ($\chi'$) a.c. susceptibility of 2 at several temperatures between 1.8 and 11 K. Right: Cole-Cole diagrams for 2 at different temperatures between 2 and 8.5 K.
**Fig. S6.** Frequency dependence at 4 K of the in-phase ($\chi'$) (left) and out-of-phase ($\chi''_M$) (right) a.c. susceptibility of 2 under several d.c.-fields from 0 to 8000 G.

**Fig. S7.** Argand plots for 2 at 4 K in several d.c.-fields.

**Fig. S8.** Field dependence of the magnetization for 2 at the field sweep rate of 0.14 T/s and temperatures between 0.04 and 5 K.
**Fig. S9.** Plots of (left) $\chi'$ vs. $T$ in zero-d.c. field and (right) $\chi''$ vs. $T$ in 5kG dc field, for 1a/1b, at several frequencies between 2 and 1202 Hz.

**Fig. S10.** Frequency dependence of the (left) in-phase ($\chi'$) and (right) out-of-phase ($\chi''$) ac susceptibility of 1a/1b at temperatures between 2 and 25 K.

**Fig. S11.** Left: Cole-Cole plots for 1a/1b at temperatures between 3 and 25 K and zero d.c.-field. Right: Fits of Cole-Cole plots at 7 and 8 K as a sum of two modified Debye processes, with $\tau_{1a}$ (ms)/$\tau_{1b}$ (ms)/$\alpha_{1a}$/$\alpha_{1b}$ = 0.27 / 163.7/ 0.33 / 0.11 at 7 K and 0.15 / 78.6 / 0.33 / 0.12 at 8 K.