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Supporting information for:

A Half-sandwich Organometallic Single-Ion Magnet with Hexamethylbenzene Coordinating to the Dy(III) Ion

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Synthesis

General Considerations

All manipulations and syntheses described below were performed under an argon or dinitrogen atmosphere without coordinating solvents using standard Schlenk line, high vacuum line, glovebox techniques and H-Shaped tube. Toluene was sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Elemental analyses (C, H, N) were conducted on a Perkin-Elmer 2400 Series II CHNS elemental analyzer. Anhydrous LnCl₃ (Ln= Dy, Tb) was purified according to literature.¹ Anhydrous AlCl₃ was purchased from Alfa Aesar and used as received. Hexamethylbenzene was purchased from Acros Organics and dried under high vacuum overnight before use.

Synthesis of [(C_6Me_6)**Dy**(**AlCl**₄)₃], **Dy complex.** The procedure followed the literature method² with two manipulations modified. Firstly, the reaction was carried out in an H-shaped tube which was sealed during the reaction, and the hot solution in one side of the H-shaped tube was quickly filtered into the other side, which can get rid of the precipitation problem caused by temperature decrease during centrifugation. Secondly, the single crystals were grown from the hot toluene solution by decreasing the temperature from 70 to 60 to 50 °C sequentially instead of cooling to the room temperature directly. Detailed manipulations are described below. Anhydrous DyCl₃ (54 mg, 0.2 mmol), anhydrous AlCl₃ (80 mg, 0.6 mmol) and C₆Me₆ (39 mg, 0.24 mmol) were added into one side of an H-shaped tube, followed by addition of 10 mL toluene. The H-shaped tube was sealed with a Teflon stopcock and the mixture was stirred for 3 days at the temperature range 90-95 °C. The yellow solution was filtered into the other side of the H-tube, and the temperature was decreased to get single crystals suitable for X-ray diffraction. Almost colorless pale yellow single crystals of **Dy complex** (35 mg, 21%) were collected from the yellow solution. Anal. Calcd for C₁₂H₁₈DyAl₃Cl₁₂: C 17.34, H 2.18; Found: C 17.54, H 2.39.

Synthesis of $[(C_6Me_6)Tb(AlCl_4)_3]$, Tb complex. The procedure was as same as above. Almost colorless pale yellow single crystals of Tb complex (45 mg, 27%) were collected from the yellow solution. Anal. Calcd for $C_{12}H_{18}TbAl_3Cl_{12}$: C 17.42, H 2.19; Found: C 17.53, H 2.37.

Crystal Structure Determination

X-ray Data Collection, Structure Solution and Refinement for $[(C_6Me_6)Dy(AlCl_4)_3]$, Dy complex.

A colorless crystal of approximate dimensions 0.112 x 0.165 x 0.333 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2³ program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT⁴ and SADABS⁵ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁶ program. There were neither systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group P_{-1} was assigned and later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques⁷. The analytical scattering factors⁸ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

At convergence, wR2 = 0.0388 and Goof = 1.037 for 259 variables refined against 6423 data (0.75Å), R1 = 0.0163 for those 6105 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for [(C₆Me₆)Tb(AlCl₄)₃], Tb complex.

A colorless crystal of approximate dimensions 0.208 x 0.240 x 0.336 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2³ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT⁴ and SADABS⁵ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁶ program. There were neither systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group P_{-1} was assigned and later determined to be correct. The structure was solved using the coordinates of the dysprosium analogue and refined on F² by full-matrix least-squares techniques⁷. The analytical scattering factors⁸ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

At convergence, wR2 = 0.0434 and Goof = 1.037 for 259 variables refined against 6767 data (0.74Å), R1 = 0.0168 for those 6523 data with $I > 2.0\sigma(I)$.

Definitions:

 $wR2 = \left[\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\right]^{1/2}$

 $R1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$

Goof = $S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

The crystal data information for complexes are summarized in Table S1 and S2. CCDC 1005795 (**Dy complex**) and 1005794 (**Tb complex**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Properties Measurements

A powder sample obtained by crushing from crystals was fixed in the NMR tube within eicosane and parafilm to avoid moving during the magnetic measurements. The NMR tube was sealed in vacuum to protect samples from air. Measurements for dc magnetic properties of the **Dy** and **Tb** complexes were performed on a Quantum Design MPMSXL-5 SQUID magnetometer. Magnetic data were corrected with eicosane, parafilm, NMR tube and Pascal constants. Measurements of alternating current (ac) susceptibilities were carried out in the 100–10000 Hz frequency range using Quantum Design PPMS-9T. And the measurements of hysteresis loops for **Dy** complex were conducted on PPMS-VSM.

Ab initio calculations for the Dy and Tb complexes.

Complete-active-space self-consistent field (CASSCF) calculations on individual lanthanide fragments have been carried out with MOLCAS 7.8 program package.⁹ In all calculations, we used the complete structures of the **Dy** and **Tb** complexes shown in Figure 1 and S7. The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for Ln (Tb^{III}, Dy^{III}) ions; VTZ for close Cl and C; VDZ for distant atoms. The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set and the spin-orbit coupling was handled separately in the restricted active space state interaction (RASSI-SO) procedure. For each complex, the active electrons in 7 active spaces include all f electrons in the CASSCF calculation. We have mixed the maximum number of the spin-free state which was possible with our hardware (Tb, 215; Dy, 279).

Formula	$C_{12}H_{18}DyAl_3Cl_{12}\\$	$C_{12}H_{18}TbAl_3Cl_{12}$
fw	831.10	827.52
Crystsyst	Triclinic	Triclinic
spacegroup	$P \overline{1}$	$P \overline{1}$
<i>a</i> , Å	9.5626(5)	9.5934(5)
b, Å	9.6465(5)	9.6912(5)
<i>c</i> , Å	17.8181(10)	17.8558(10)
α, °	93.3339(6)	93.2661(6)
<i>β</i> , °	97.4937(6)	97.3859(6)
γ, °	119.6077(5)	119.6522(5)
<i>V</i> , Å ³	1402.42(13)	1416.64(13)
Ζ	2	2
<i>Т</i> , К	143(2)	143(2)
<i>F</i> (000)	798	796
μ , mm ⁻¹	3.904	3.723
λ, Å	0.71073	0.71073
$R1 [I \ge 2\sigma(I)]$	0.0163	0.0168
wR2 (all data)	0.0388	0.0434
S	1.037	1.037

Table S1. X-ray Data Collection Parameters for [(C₆Me₆)Dy(AlCl₄)₃] and [(C₆Me₆)Tb(AlCl₄)₃].

Table S2. Bond Lengths [Å] and Angles [°] for [(C₆Me₆)Dy(AlCl₄)₃] and [(C₆Me₆)Tb(AlCl₄)₃]

Formula	$C_{12}H_{18}DyAl_3Cl_{12}\\$	C12H18TbAl3Cl12
Ln-Cent	2.471	2.488
Ln-Cl(1)	2.8168(5)	2.8261(5)
Ln-Cl(2)	2.8256(5)	2.8382(5)
Ln-Cl(5)	2.7947(5)	2.8061(4)
Ln-Cl(6)	2.7911(5)	2.8107(5)
Ln-Cl(9)	2.7860(5)	2.7993(4)
Ln-Cl(10)	2.7916(5)	2.8034(5)
Ln-C(1)	2.8338(19)	2.8453(18)
Ln-C(2)	2.8885(19)	2.9025(19)
Ln-C(3)	2.8733(19)	2.8831(19)
Ln-C(4)	2.8528(19)	2.8670(19)
Ln-C(5)	2.8290(19)	2.8527(19)
Ln-C(6)	2.7993(18)	2.8170(18)
Cnt-Ln-Cl(1)	103.1	103.2
Cnt-Ln-Cl(2)	102.3	102.2
Cnt-Ln-Cl(5)	100.4	100.5
Cnt-Ln-Cl(6)	173.9	173.7
Cnt-Ln-Cl(9)	105.4	105.6
Cnt-Ln-Cl(10)	99.9	100.0



Fig. S1. *M*(*H*) plots for the Dy complex (left) and the Tb complex (right) at 2 K.



Fig. S2. *M*(*HT*⁻¹) plots for the Dy complex (left) and the Tb complex (right) at 2, 3, 5, 8 and 10 K.



Fig. S3. Temperature dependence of ac magnetic susceptibility properties of the Dy complex without static field.



Fig. S4. The plot of τ vs *H* at 9.0 K for the Dy complex. A 2 kOe dc field was selected to do the further measurements as shown in Fig. 2 and Fig. S5.



Fig. S5. Temperature dependence of ac magnetic susceptibility properties of the Dy complex with a 2 kOe dc field.



Fig. S6. Hysteresis loop of the Dy complex at 2.5 K and 3.0 K with a 200 Oe/s sweep rate of the magnetic field.



Fig. S7. Thermal ellipsoid plot of [(C₆Me₆)Tb(AlCl₄)₃] drawn at the 50% probability level. Selected bond lengths [Å]: Tb-C, 2.8170(18)-2.9025(19), Tb-Centroid (HMB), 2.488, Tb-C(average), 2.861, Tb-Cl, 2.7993(4)-2.8382(5), Tb-Cl(average), 2.814. Hydrogen atoms are omitted for clarity.



Fig. S8. Temperature dependence of ac magnetic susceptibility properties of the Tb complex without static field.



Fig. S9. The calculated easy axis orientation (red arrow) of the **Tb** complex viewed perpendicular (left) and parallel (right) to the Tb(III)-centroid (HMB) direction. Hydrogen atoms are omitted for clarity.

Parameter	Dy	Tb
g_x	0.0145	0.0000
g_y	0.0258	0.0000
g_z	19.6985	16.4483
Charge(Ln)	1.27	1.26
Charge(C1)	-0.26	-0.26
Charge(C2)	-0.24	-0.24
Charge(C3)	-0.27	-0.26
Charge(C4)	-0.27	-0.27
Charge(C5)	-0.23	-0.22
Charge(C6)	-0.26	-0.25
Charge(Cl1)	-0.46	-0.46
Charge(Cl2)	-0.43	-0.43
Charge(Cl5)	-0.45	-0.45
Charge(Cl6)	-0.38	-0.38
Charge(Cl9)	-0.44	-0.44
Charge(Cl10)	-0.43	-0.43
Charge(Al1)	0.94	0.95
Charge(Al2)	0.95	0.95
Charge(Al3)	0.95	0.95

Table S3. Calculated *g* Values of the Low-lying Ground States, and Mulliken Charge Population of Selected Atoms for the Dy and Tb Complexes.

No.	Dy	Tb
1	0	0
2	80.4	0.1
3	90.6	22.7
4	97.4	23.1
5	120.1	45.9
6	135.8	47.4
7	151.3	80.5
8	173.3	82.9
9		88.1
10		88.3
11		105.7
12		122.7
13		128.4

Table S4. Calculated Energies (cm⁻¹) of the Low-lying States for the Dy and Tb complexes.

References

- 1. M. D. Taylor and C. P. Carter, J. Inorg. Nucl. Chem., 1962, 24, 387.
- (a) F. A. Cotton and W. Schwotzer, J. Am. Chem. Soc., 1986, 108, 4657; (b) H. Liang, Q. Shen, J. Guan and Y. Lin, J. Organomet. Chem., 1994, 474, 113.
- 3. APEX2 Version 2012.4-0, Bruker AXS, Inc.; Madison, WI 2012.
- 4. SAINT Version 7.68a, Bruker AXS, Inc.; Madison, WI 2009.
- 5. Sheldrick, G. M. SADABS, Version 2008/1, Bruker AXS, Inc.; Madison, WI 2008.
- 6. Sheldrick, G. M. SHELXTL, Version 2013/1, Bruker AXS, Inc.; Madison, WI 2013.
- 7. Sheldrick, G. M. SHELXTL, Version 2013/3, Bruker AXS, Inc.; Madison, WI 2013.
- 8. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.
- 9. G. Karlström, R. Lindh, P.-Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady and L. Seijo, *Comput. Mater. Sci.*, 2003, **28**, 222.