CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

# A Non-sandwiched Macrocyclic Monolanthanide Single-Molecule Magnet: The Key Role of Axiality

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**Synthesis of [$Zn_3Dy(L^{Pr})(NO_3)_3(MeOH)_3$]·4$H_2O$** (**2**·4$H_2O$): To a solution of **1** (0.030 g, 0.18 mmol) in methanol (5 mL) was added a solution of $Zn(OAc)_2$·2$H_2O$ (0.040 g, 0.18 mmol) and $Dy(NO_3)_3$·6$H_2O$ (0.026g, 0.06 mmol) in methanol (10 mL), resulting in an orange solution. After stirring this solution for ten minutes, 1,3-diaminopropane (0.014 g, 0.18 mmol) in methanol (5 mL) was added dropwise. This reaction was stirred for a further ten minutes before being left to stand overnight. Diethyl ether was vapour diffused into the orange solution. The resulting solid was filtered, washed with diethyl ether and dried in air giving [$Zn_3Dy$(**$L^{Pr}$**)$(NO_3)_2(MeOH)_3$]($NO_3$)·4$H_2O$ as an orange powder (0.056 g, 71%). Found: C, 32.77; H, 3.55; N, 9.36. Calculated for $Zn_3DyC_{36}H_{50}N_9O_{22}$: C, 32.77; H, 3.82; N, 9.55. IR (KBr disk) ? / $cm^{-1}$ = 3420 (b); 1627 (sh); 1521 (w); 1459 (sh); 1383 (sh); 1329 (sh); 1235 (sh); 1177 (sh); 730 (w); 668 (w); 611 (w).

**Crystal data for [$Zn_3Dy(L^{Pr})(NO_3)_3(MeOH)_3$]·1.5MeOH·$H_2O$:** Triclinic, P-1, orange rod, a = 12.4698(15), ß = 13.2401(18), ? = 16.989(3), a = 98.859(3), b = 107.259(3), c = 110.248(3), V = 2403.4(6), Z = 2. 49862 Reflections collected at 91 K. The structure was solved by direct methods using SHELXS-97[1] and refined against all $F^2$ data (SHELXL)[1] to $R^1$ of 0.0535 for 8192 data with $F > 4s(F)$; $wR^2$ = 0.1432, GOF = 1.039 for all 9704 unique reflections. For further details see the cif file. CCDC 780637.

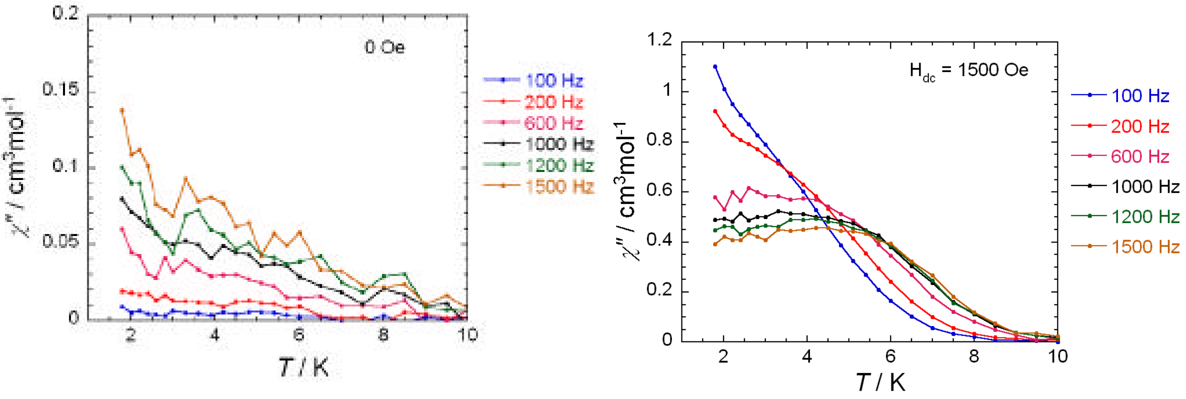

Figure S1: (Left) The out-of-phase component to the AC susceptibility of **2**·4$H_2O$ in a zero DC field. (Right) The out-of-phase component to the AC susceptibility in a 1500 Oe DC field, showing enhancement of frequency dependence.

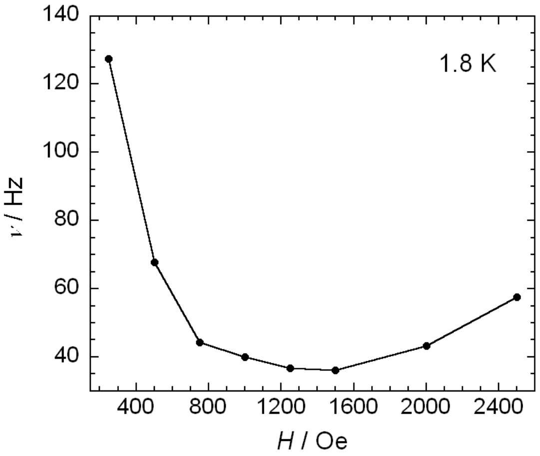

Figure S2: DC field dependence of the frequency at 1.8 K for **2**·4$H_2O$. The solid line is a guide for the eye.

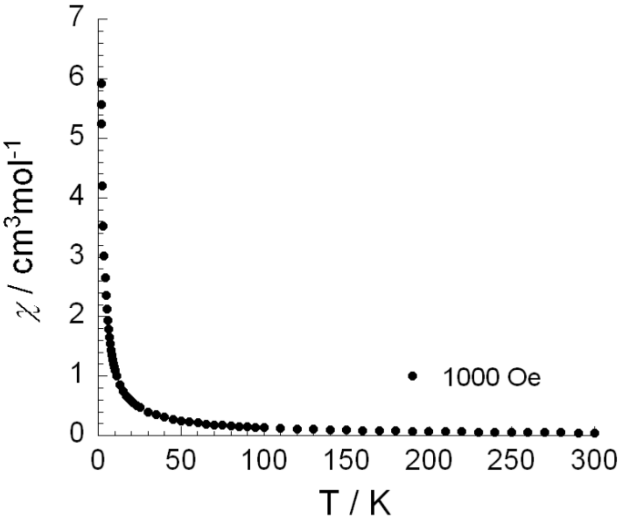

Figure S3: ? vs T for **2**·4$H_2O$.

## Computational details

The magnetic properties of dysprosium center in the $DyZn_3$ complex has been studied by ab initio calculations by using a specially designed routine SINGLE_ANISO[2] interfaced with the MOLCAS package.[3] The full molecule was computed, using the structure obtained in the X-ray experiments. The basis sets used for the calculations were taken from ANO-RCC basis library from MOLCAS package.[4]

For the electronic structure, the *ab initio* calculations were performed by means of MOLCAS-7.4 program.[3] The active space for the complete active space self-consisting field (CASSCF) calculation of the dysprosium fragment included the 4f orbitals (CAS (9 in 7)) since we are interested in the ligand field states only.

Since the lanthanides have a very strong spin-orbit coupling, a large number of roots should be included in the spin-orbit mixing within the restricted active space state interaction (RASSI-SO) procedure.[6] To avoid convergence problems we had to include in the self-consistent CASSCF calculation all possible roots available for a given active space, but we could mix by spin-orbit interaction only a limited amount of terms. We took in this mixing all roots up to 50000 $cm^{-1}$. The number and free ion parentage of states mixed by RASSI are listed together with the fragment description below.

With the obtained spin-orbit multiplets, the powder susceptibility and the g-tensors for the lowest Kramers doublets of the molecule were further evaluated using the recently developed *ab initio* methodology.[2] The basis of this approach is the *ab initio* calculation of all orbital moment and magnetic moment matrix elements on the relevant spin-orbit multiplets obtained in CASSCF/CASPT2 calculations. These matrix elements are used in a separate routine to calculate:

(i) magnetic properties measured directly in experiment (temperature dependent Van Vleck susceptibility tensor and powder averaged function, field-dependent magnetisation for different temperatures and directions and the powder magnetisation) and

(ii) parameters of magnetic spin Hamiltonians for different spin-orbit multiplets and groups of spin states, described by the corresponding pseudospin, (*g* tensors, zero-field splitting tensors, etc).

In calculations of magnetic properties, all spin-orbit multiplets of ligand-field type on the metal sites are usually taken into account, in particular. This was found to be important for correct quantitative description of the effects of strong magnetic anisotropy and strong applied magnetic fields. Computationally, this routine (SINGLE_ANISO) was interfaced with MOLCAS-7.4 program.

*Basi Sets:*
Dy -- 8s7p5d4f2g1h.

Zn -- 5s4p2d1f.
O -- 4s3p1d. (close)
N -- 4s3p1d.(close)
O,N,C, -- 3s2p. (distant)
H – 2s.
There were 963 basis functions.

*Active space:*
CAS(9 in 7)

*Roots mixed in RASSI:*
All the states coming from the following multiplets have been taken into account in the spin-orbit interaction (RASSI):
$^6$H, $^6$F, $^6$P (all sextets), $^4$I, $^4$F, $^4$M, $^4$G, $^4$L, $^4$D, $^4$H, $^4$P, $^4$G, $^4$F, $^4$I (128 out of 224 quartets), $^2$L, $^2$K, $^2$P, $^2$N, $^2$F, $^2$M, $^2$H, $^2$D, $^2$G, $^2$O (130 out of 490 doublets).

**Table 1**. Calculated energies of the lowest spin free states and the resulting energies of spin-orbit Kramers doublets (cm$^{-1}$).

| Free ion multiplets | CASSCF | Spin-Orbit KD |
|---|---:|---:|
| 6H | 0.000 | 0.000 |
| | 29.141 | 41.656 |
| | 88.324 | 75.414 |
| | 95.610 | 217.659 |
| | 173.780 | 273.593 |
| | 192.913 | 298.865 |
| | 365.422 | 343.111 |
| | 387.092 | 391.886 |
| | 497.258 | 3600.919 |
| | 538.556 | 3638.170 |
| | 581.656 | 3656.924 |
| 6F | 7545.280 | 3757.648 |
| | 7689.865 | 3792.710 |
| | 7716.568 | 3833.958 |
| | 7748.056 | 3867.055 |
| | 7790.342 | 6144.912 |
| | 7825.409 | 6174.604 |
| | 7839.168 | 6196.448 |
| 6P | 34895.722 | 6284.225 |
| | 34973.301 | 6318.102 |
| | 35318.625 | 6392.205 |
| 4 | 24863.541 | 8104.800 |
| | 24867.814 | 8122.593 |
| | 24888.265 | 8168.407 |
| | 24929.672 | 8271.952 |
| | 24939.548 | 8335.028 |
| | 24950.824 | 9631.063 |
| | 24968.671 | 9668.974 |
| | 25026.846 | 9702.661 |
| | … | 9890.693 |
| 2 | 37341.733 | 10009.283 |
| | 37348.122 | 10087.199 |
| | 37382.833 | 10113.279 |
| | 37384.461 | 10127.213 |
| | 37389.024 | 10142.449 |
| | 37404.025 | 10167.062 |
| | 37424.148 | 10779.970 |
| | 37439.125 | 10911.285 |
| | 37529.913 | 10990.807 |
| | 37565.644 | 11477.816 |
| | ... | 11516.948 |
| | | 11547.755 |
| | | 11557.745 |
| | | 11571.142 |
| | | 13401.393 |
| | | … |

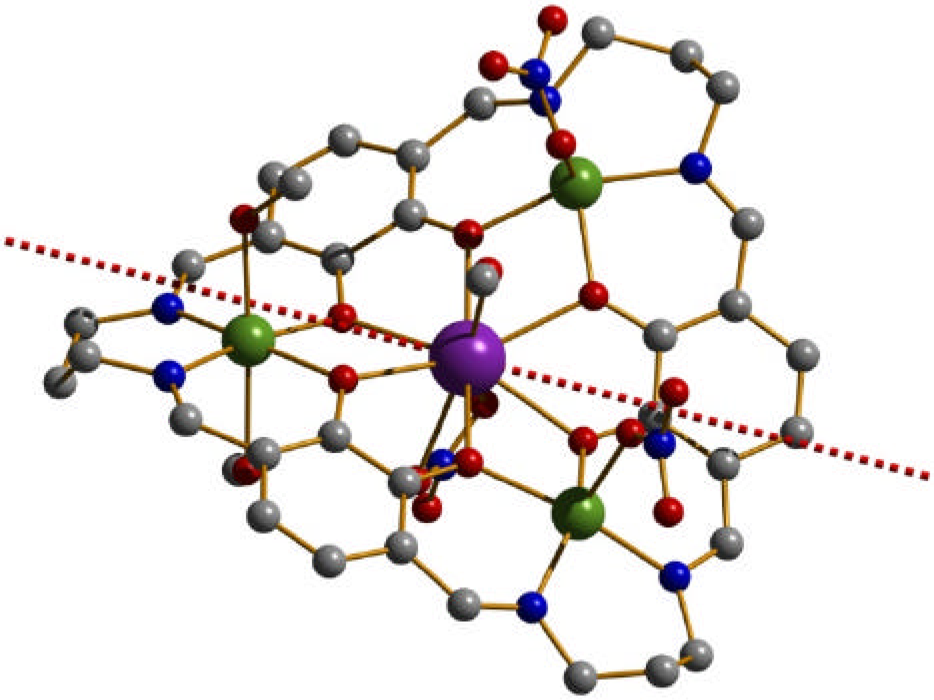

Figure S4: The structure of the **calculated** $DyZn_3$ complex (i.e. full molecule). The hydrogens have been removed for clarity. The **red dashed line** shows the orientation of the **main anisotropy axis** of the $DyZn_3$ complex. Color scheme: Dy-violet, Zn-green, N-blue, C-grey, O-red.

The intermolecular interaction is $zJ = +\ 0.005\ \mathrm{cm}^{-1}$.

## References

[1] G. M. Sheldrick, G. M. Sheldrick, *Acta Crystallogr., Sect. A*, **2008**, *A64*, 112.

[2] L. F. Chibotaru, L. Ungur, Program SINGLE_ANISO, University of Leuven 2006.

[3] G. Karlström, R. Lindh, P. -Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P. -O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, L. Seijo, *Comp. Mater. Sci.* **2003**, *28*, 222-239.

[4] K. Pierloot, B. Dumez, P.-O. Widmark and B. O. Roos, *Theor. Chim. Acta* **1995**, *90*, 87.; B. O. Roos, R. Lindh, P-O. Malmqvist,V. Veryazov V., P. O. Widmark, *J. Phys. Chem. A*, **2004**, *108*, 2851.

[5] B. O. Roos, P-O. Malmqvist, *Phys. Chem. Chem. Phys.* **2004**, *6*, 2919-2927.

[6] L. Ungur, W. Van den Heuvel, L.F. Chibotaru, *New J. Chem.* **2009**, *33*, 1224-1230.

# checkCIF/PLATON report (basic structural check)

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No syntax errors found.                              CIF dictionary
Please wait while processing ....                    Interpreting this report
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## Datablock: hf499

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Bond precision:  C-C = 0.0099 A          Wavelength=0.71073
Cell:        a=12.4698(15)  b=13.2041(18)  c=16.989(3)
             alpha=98.697(7)beta=107.380(7)gamma=110.144(5)
Temperature:91 K
                Calculated                Reported
Volume          2403.4(6)                 2403.4(6)
Space group     P -1                      P-1
Hall group      -P 1                      ?
Moiety formula  2(C37 H45 Dy N9 O19 Zn3), ?
                H4 O2, C H4 O
Sum formula     C75 H98 Dy2 N18 O41 Zn6   C37.50 H49 Dy N9 O20.50
                                          Zn3
Mr              2625.06                   1312.47
Dx,g cm-3       1.814                     1.814
Z               1                         2
Mu (mm-1)       3.103                     3.103
F000            1314.0                    1314.0
F000'           1315.90
h,k,lmax        15,16,21                  15,16,21
Nref            9978                      9704
Tmin,Tmax       0.646,0.830               0.477,0.836
Tmin'           0.415
Correction method= MULTI-SCAN
Data completeness= 0.973  Theta(max)= 26.510
R(reflections)=             wR2(reflections)=
0.0535( 8192)               0.1432( 9704)
S = 1.039         Npar= 631
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The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

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**Alert level B**

PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) ....... 3
PLAT220_ALERT_2_B Large Non-Solvent O Ueq(max)/Ueq(min) ... 4.16 Ratio
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for O16
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for O18
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for N12A
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for N12B
PLAT417_ALERT_2_B Short Inter D-H..H-D H70X .. H90X .. 1.94 Ang.

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**Alert level C**

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PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low .......       0.97
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density ....       3.15
PLAT242_ALERT_2_C Check Low       Ueq as Compared to Neighbors for      Zn3A
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds (x 1000) Ang ..        10
PLAT041_ALERT_1_C Calc. and Reported SumFormula    Strings  Differ         ?
PLAT045_ALERT_1_C Calculated and Reported Z Differ by ............      0.50 Ratio
PLAT480_ALERT_4_C Long H...A H-Bond Reported H80Y   ..  O90     ..      2.77 Ang.
PLAT481_ALERT_4_C Long D...A H-Bond Reported O80    ..  O90     ..      3.63 Ang.
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #         2
          H4 O2
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #         3
          C H4 O
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**Alert level G**

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PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.      18.45
PLAT301_ALERT_3_G Note: Main Residue  Disorder ..................       8.00 Perc.
PLAT343_ALERT_2_G Check sp?     Angle Range in Main Residue for ..       C19
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints .......        18
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..................      50.00 Perc.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF ......     23.61 Deg.
          ZN3A -O4   -ZN3B    1.555   1.555   1.555
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF ......     23.44 Deg.
          ZN3B -N4   -ZN3A    1.555   1.555   1.555
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF ......     23.26 Deg.
          ZN3A -N5   -ZN3B    1.555   1.555   1.555
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          N12B -O16  -N12A    1.555   1.555   1.555
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          N12A -O18  -N12B    1.555   1.555   1.555
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF ......     33.20 Deg.
          H80Y -O80  -H81X    1.555   1.555   1.555
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF ......     24.60 Deg.
          H80Y -O81  -H81X    1.555   1.555   1.555
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 0 ALERT level A = In general: serious problem
 7 ALERT level B = Potentially serious problem
10 ALERT level C = Check and explain
13 ALERT level G = General alerts; check

 2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
11 ALERT type 2 Indicator that the structure model may be wrong or deficient
 4 ALERT type 3 Indicator that the structure quality may be low
13 ALERT type 4 Improvement, methodology, query or suggestion
 0 ALERT type 5 Informative message, check
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# **Datablock hf499** - ellipsoid plot

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