

Supporting Information

Twists to the spin structure of the Ln₉-diabolo motif exemplified in two {Zn₂Ln₂}[Ln₉]{Zn₂} coordination clusters

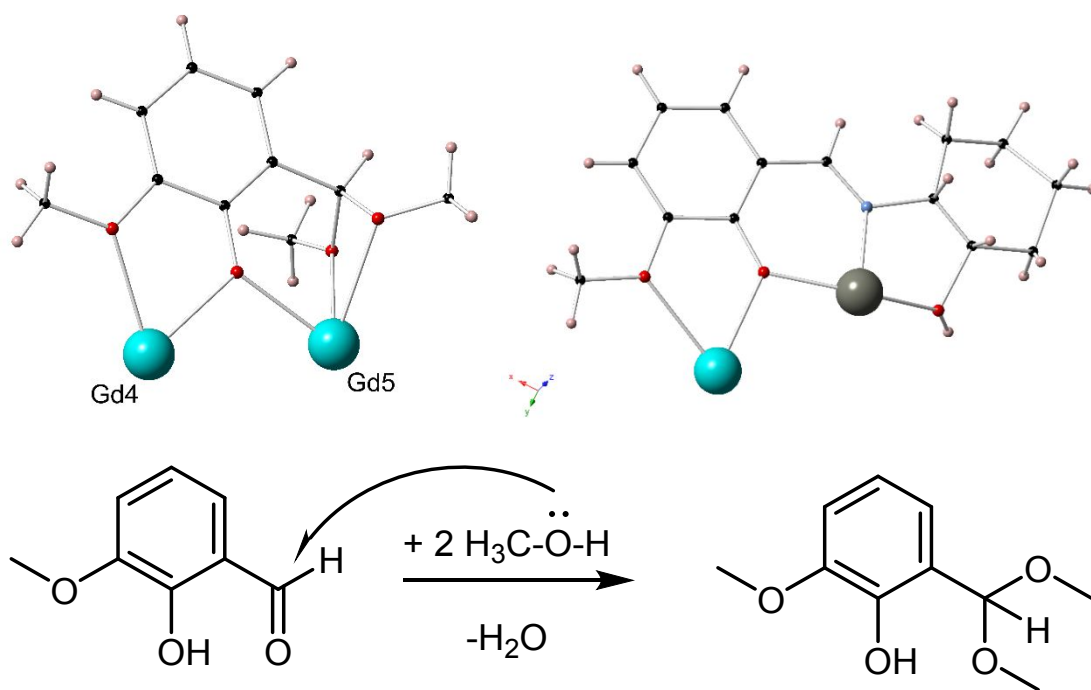
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Scheme S1. (upper) The coordination modes of the organic ligands observed in **1** and **2**. (lower)

A plausible mechanism for the in situ formation of HL3.

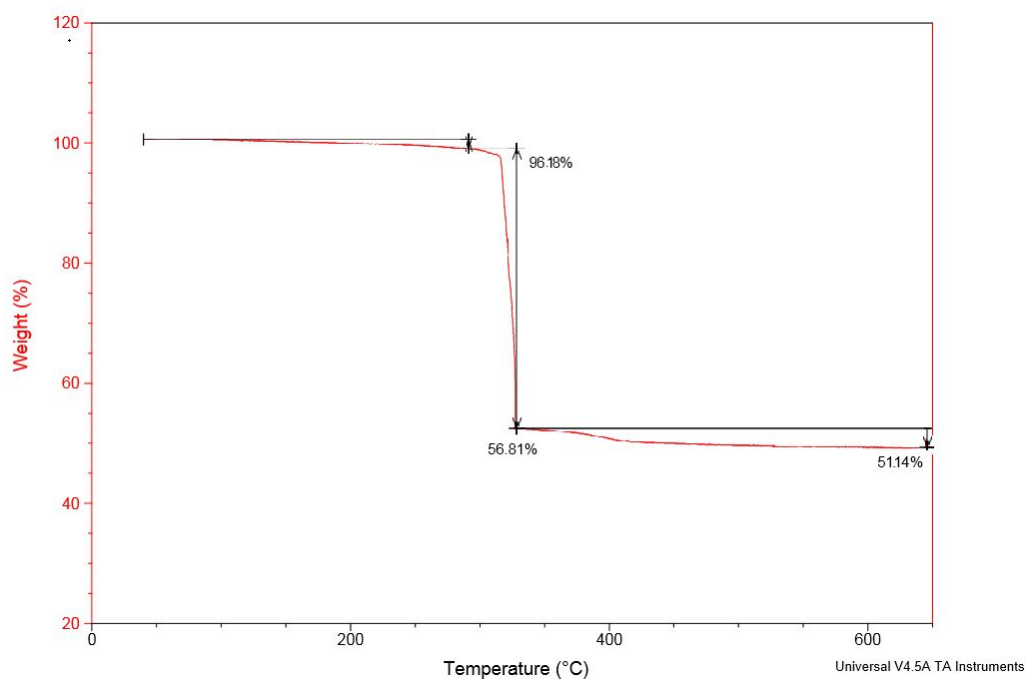


Figure S1 TGA of compound **1**.

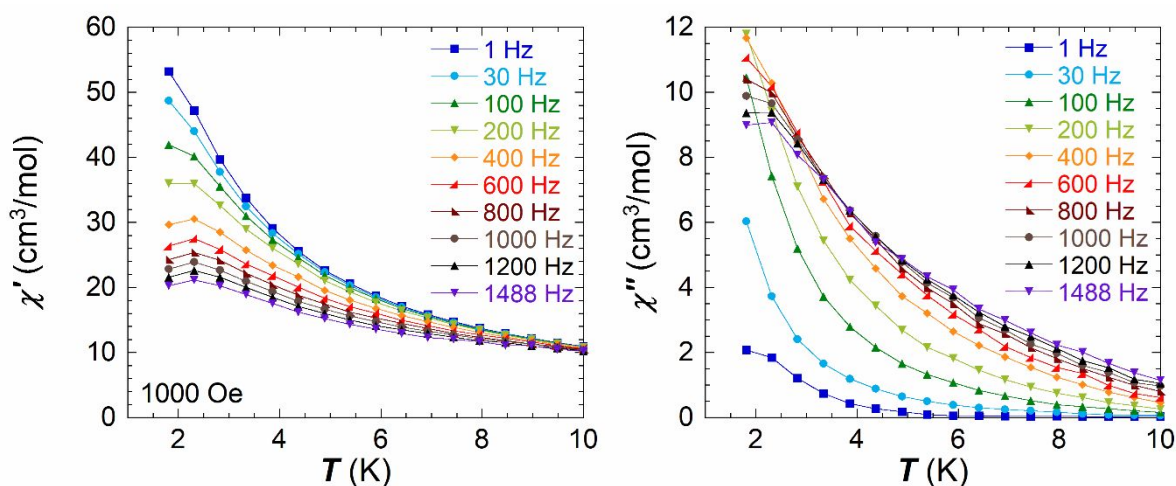


Figure S2. Temperature dependence of the in-phase χ_M' (left) and out-of phase χ_M'' (right) susceptibility for $\text{Zn}_4\text{Dy}_{11}$ (2) at different frequencies under an applied field of 1000 Oe.

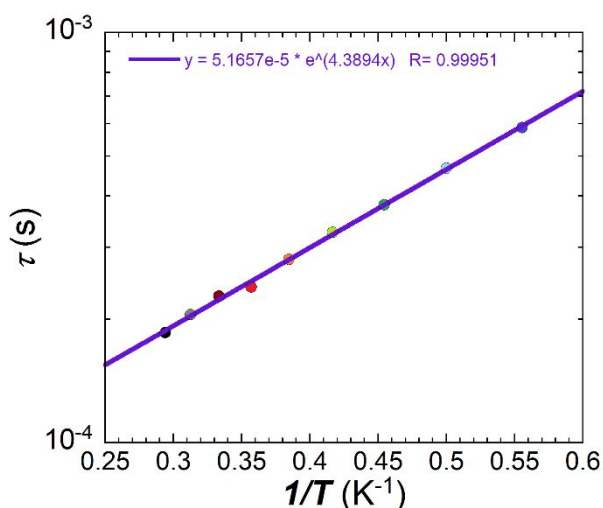


Figure S3. Arrhenius fit for $\text{Zn}_4\text{Dy}_{11}$ (2), leading to $U_{\text{eff}} = 4.4$ K and $\tau_0 = 5.2 \cdot 10^{-5}$ s ($R = 0.99$).

SHAPE Analysis^[1]

Ln3 to Ln5 have a nitrate anion to fulfil their coordination sphere, where the Ln-N bond is within the range of 2.90-2.96 Å, and are therefore not considered. In case of Ln2 and Ln6 which are linked together via two nitrate groups, the Ln-N bond is shortened to 2.84 Å, but with the electron density coming most from the oxygens, these Ln-N are not considered, either. Ln2 to Ln5 and Ln2' to Ln5' which are generated by symmetry operation, respectively, are surrounded by nine oxygens, while Ln1, which is the metal ion located in the centre of the sandglass, and the two Ln6 metal ions, which are part of the tetranuclear handle bar, are only eight-coordinated. It appears here that from the SHAPE analysis Gd3/Dy4 resemble each other, such as Gd4/Dy3,

respectively. A similar behaviour occurs for Gd2/ Dy5, and Dy2/ Gd5 respectively. This is a simple a consequence of having refined **2** anticlockwise in comparison to **1**. The 9-coordinated Ln^{III} ions are close to a spherical capped square antiprism (CSAPR-9 in Table S2), with a deviation between 1.41-1.87% from the perfect geometry, although in case of Gd3, the surrounding atoms are closer to a muffin topology with a deviation of 1.34%. Gd6 is more distorted in the coordination environment and the smallest deviation was found to be biaugmented trigonal prismatic (BTPR-8 in Table S3) with a deviation of 3.86%.

Table S1. Complete results of the SHAPE analysis for the nine-coordinated Ln^{III} ions in complex Zn₄Gd₁₁ (1) and Zn₄Dy₁₁ (2) with EP-9 = enneagon, OPY-9 = octagonal pyramid, HBPY-9 = heptagonal bipyramid, JTC-9 = Johnson triangular cupola, JCCU-9 = capped cube, CCU-9 = spherical-relaxed capped cube, JCSAPR-9 = Capped square antiprism, CSAPR-9 = spherical capped square antiprism, JTCTPR-9 = tricapped trigonal prism, TCTPR-9 = spherical tricapped trigonal prism, JTDIC-9 = tridiminished icosahedron, HH-9 = hula-hoop, MFF-9 = muffin.

| | Gd2 | Dy2 | Gd3 | Dy3 | Gd4 | Dy4 | Gd5 | Dy5 |
|----------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| EP-9 | 32.856 | 33.888 | 34.682 | 34.719 | 34.565 | 34.966 | 33.790 | 32.915 |
| OPY-9 | 19.651 | 19.374 | 23.307 | 22.957 | 23.033 | 23.182 | 19.256 | 19.579 |
| HBPY-9 | 17.313 | 18.063 | 18.576 | 17.810 | 17.867 | 18.510 | 18.131 | 17.306 |
| JTC-9 | 13.795 | 14.903 | 14.341 | 14.070 | 14.022 | 14.445 | 14.826 | 13.782 |
| JCCU-9 | 9.709 | 10.621 | 10.392 | 9.305 | 9.187 | 10.279 | 10.719 | 9.799 |
| CCU-9 | 9.037 | 9.625 | 9.787 | 9.063 | 8.946 | 9.694 | 9.747 | 9.126 |
| JCSAPR-9 | 2.535 | 2.453 | 1.869 | 1.952 | 2.077 | 1.863 | 2.449 | 2.560 |
| CSAPR-9 | 1.873 | 1.674 | 1.411 | 1.493 | 1.526 | 1.426 | 1.680 | 1.881 |
| JTCTPR-9 | 3.609 | 3.814 | 2.336 | 2.196 | 2.234 | 2.345 | 3.774 | 3.650 |
| TCTPR-9 | 2.326 | 1.953 | 2.257 | 2.158 | 2.140 | 2.234 | 1.972 | 2.297 |
| JTDIC-9 | 11.417 | 11.292 | 12.087 | 11.642 | 11.739 | 12.280 | 11.351 | 11.451 |
| HH-9 | 10.955 | 11.810 | 11.480 | 11.370 | 11.413 | 11.374 | 11.867 | 10.978 |
| MFF-9 | 2.070 | 2.023 | 1.345 | 1.694 | 1.688 | 1.326 | 2.055 | 2.077 |

Table S2 Complete results of the SHAPE analysis for the eight-coordinated Ln^{III} ions in complex Zn₄Gd₁₁ (1) and Zn₄Dy₁₁ (2) with OP-8 = octagon, HPY-8 = heptagonal pyramid, HBPY-8 = hexagonal bipyramid, CU-8 = cube, SAPR-8 = square antiprism, TDD-8 = triangular dodecahedron, JGBF-8 = Johnson gyrobifastigium, JETBPY-8 = Johnson elongated triangular bipyramid, JBTPR-8 = biaugmented trigonal prism J50, BTPR-8 = biaugmented trigonal prism, JSD-8 = snub diphendoid, TT-8 = triakis tetrahedron, ETBPY-8 = elongated trigonal bipyramid.

| | Gd6 | Dy6 | Gd1 | Dy1 |
|----------|--------------|--------------|--------------|--------------|
| OP-8 | 31.768 | 31.704 | 31.016 | 31.225 |
| HPY-8 | 23.124 | 23.055 | 23.510 | 23.441 |
| HBPY-8 | 11.900 | 11.897 | 16.622 | 16.472 |
| CU-8 | 11.657 | 11.699 | 9.222 | 9.053 |
| SAPR-8 | 5.979 | 5.957 | 0.335 | 0.372 |
| TDD-8 | 4.248 | 4.198 | 2.444 | 2.420 |
| JGBF-8 | 8.139 | 8.196 | 16.869 | 16.824 |
| JETBPY-8 | 22.734 | 22.756 | 29.112 | 29.098 |
| JBTPR-8 | 4.258 | 4.195 | 3.158 | 3.196 |
| BTPR-8 | 3.861 | 3.831 | 2.502 | 2.547 |
| JSD-8 | 4.145 | 4.106 | 5.594 | 5.615 |
| TT-8 | 12.447 | 12.495 | 10.087 | 9.920 |
| ETBPY-8 | 19.543 | 19.599 | 24.829 | 24.821 |

Table S3 Input file for Magellan program for complex Zn_4Dy_{11} (2) leading to Figure 5.

| | | | | | |
|--|----|----------|----------|----------|-------|
| Isites 11 1 2 18 20 36 37 38 39 40 41 42 | O | 5.75307 | 27.77127 | 8.20738 | -1 |
| Dy 9.36027 22.08810 7.25876 3 | O | 6.05234 | 25.13174 | 9.30001 | 0 |
| Dy 9.94045 22.08810 3.78454 3 | O | 5.41380 | 25.15733 | 7.16843 | 0 |
| O 11.03397 24.14126 3.91088 -0.33 | Dy | 10.48151 | 27.65946 | 9.03364 | 3 |
| N 11.24306 24.18858 5.20250 0 | Dy | 9.65036 | 28.72355 | 5.52165 | 3 |
| O 8.26675 24.14126 7.13243 -0.33 | Dy | 12.96595 | 29.74066 | 3.94180 | 3 |
| N 8.05766 24.18858 5.84080 0 | Dy | 9.93471 | 31.07006 | 2.55917 | 3 |
| O 9.63739 23.37475 1.79962 0 | Dy | 6.33477 | 29.74066 | 7.10151 | 3 |
| O 9.65036 20.65005 5.52165 -1 | Dy | 9.36601 | 31.07006 | 8.48413 | 3 |
| O 11.98787 21.23221 3.48814 -0.5 | Dy | 8.81921 | 27.65946 | 2.00966 | 3 |
| O 8.33567 23.11293 5.17843 -0.33 | O | 8.40357 | 30.55695 | 6.44575 | -1 |
| O 10.96505 23.11293 5.86488 -0.33 | O | 10.89715 | 30.55695 | 4.59755 | -1 |
| O 7.66207 21.46178 2.85447 0 | O | 10.75462 | 29.42908 | 7.54147 | -1 |
| O 9.85848 20.25645 2.41340 -0.5 | O | 8.54610 | 29.42908 | 3.50183 | -1 |
| O 9.66334 23.37475 9.24369 0 | O | 6.68450 | 27.27112 | 3.22244 | -0.33 |
| O 7.31285 21.23221 7.55517 -0.5 | O | 7.40024 | 25.62137 | 2.02291 | -0.33 |
| O 11.63865 21.46178 8.18883 0 | O | 9.23000 | 29.66881 | 0.83554 | -1 |
| O 9.44224 20.25645 8.62990 -0.5 | O | 8.50383 | 27.16528 | -0.49938 | 0 |
| Dy 11.74418 26.37177 3.46539 3 | O | 6.84262 | 28.17678 | 0.57138 | 0 |
| O 11.66689 25.25792 5.70298 -0.33 | N | 6.47923 | 26.10505 | 2.75420 | 0 |
| Dy 7.55654 26.37177 7.57791 3 | O | 12.24025 | 31.05149 | 2.11347 | -0.66 |
| O 7.63383 25.25792 5.34032 -0.33 | O | 13.66344 | 31.87198 | 4.30026 | -0.5 |
| O 10.99017 28.61349 2.61881 -2 | O | 14.88928 | 29.01305 | 5.30763 | -0.33 |
| O 9.54633 26.86350 4.06084 -1 | O | 15.11480 | 29.87525 | 2.50904 | 0 |
| O 11.90841 28.00049 5.09185 -1 | O | 13.40112 | 30.04313 | 6.50583 | -0.33 |
| O 10.39682 26.03004 1.59289 -1 | O | 10.73303 | 33.15757 | 2.96844 | -0.5 |
| O 13.54765 27.77127 2.83592 -1 | O | 8.38651 | 32.24210 | 4.25609 | -0.33 |
| O 13.24838 25.13174 1.74330 0 | O | 7.06047 | 31.05149 | 8.92984 | -0.66 |
| O 13.88692 25.15733 3.87487 0 | O | 8.56769 | 33.15757 | 8.07486 | -0.5 |
| O 8.31055 28.61349 8.42449 -2 | O | 10.91422 | 32.24210 | 6.78721 | -0.33 |
| O 9.75439 26.86350 6.98246 -1 | O | 11.55665 | 32.15762 | 8.88323 | -0.33 |
| O 7.39232 28.00049 5.95146 -1 | O | 9.37909 | 32.10926 | 10.83127 | 0 |
| O 8.90390 26.03004 9.45042 -1 | O | 10.07073 | 29.66881 | 10.20777 | -1 |

| | | | | |
|---|----------|----------|----------|-------|
| N | 11.78768 | 32.54982 | 7.68614 | 0 |
| O | 7.74407 | 32.15762 | 2.16007 | -0.33 |
| O | 9.92163 | 32.10926 | 0.21203 | 0 |
| N | 7.51304 | 32.54982 | 3.35716 | 0 |
| O | 12.61622 | 27.27112 | 7.82087 | -0.33 |
| O | 11.90048 | 25.62137 | 9.02039 | -0.33 |
| O | 10.79690 | 27.16528 | 11.54268 | 0 |
| O | 12.45810 | 28.17678 | 10.47192 | 0 |
| N | 12.82149 | 26.10505 | 8.28910 | 0 |
| O | 5.63728 | 31.87198 | 6.74304 | -0.5 |
| O | 4.41144 | 29.01305 | 5.73567 | -0.33 |
| O | 5.89960 | 30.04313 | 4.53747 | -0.33 |
| O | 4.18593 | 29.87525 | 8.53426 | 0 |

References

- [1] Llunell, M.; Casanova, D.; Cirera, J.; Alemany, P. and Alvarez, S. SHAPE: Program for the Stereochemical Analysis of Molecular Fragments by Means of Continuous Shape Measures and Associated Tools, Version 2.1, Barcelona, **2013**.