

# Slight Synthetic Changes Eliciting Different Topologies: Synthesis, Structure and Magnetic Properties of Novel Dinuclear and Nonanuclear Dysprosium Complexes.

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## Supporting Information

### Experimental

#### Synthesis of ligand and compounds

1,5-Bis(2-hydroxy-3-methoxybenzylidene)carbonohydrazide (H<sub>2</sub>hmc)

To a mixture of carbonyldrazine (0.005 mol, 0.450 g) in ethanol (20 mL) was added a solution of *o*-vanillin (0.010 mol, 1.52 g) in ethanol (20 mL). The mixture was stirred and refluxed overnight. The product, a white powder, was filtered, washed with cold ethanol and dried in vacuo. Yield = 78%. NMR (DMSO-*d*<sub>6</sub>, 400 Mhz): 10.85 (s, 2H), 8.42 (s, 2H), 7.30 (s, 2H), 6.98 (d, 2H), 6.82 (t, 2H), 3.80 (s, 6H), 3.34 (s, 2H). IR (KBr, cm<sup>-1</sup>): 3242 (m), 3064 (w), 3004 (w), 1685 (s), 1614 (w), 1548 (m), 1469 (m), 1416 (w), 1351(w), 1299(m), 1253(s) 1147 (w), 1082 (m), 1026 (w), 974 (m), 837 (w), 777 (m), 730 (m)..

[Dy<sub>2</sub>(Hhmc)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·THF·MeCN (**1**).

To a solution of Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.5 mmol, 0.228g) in MeCN (15 mL) was added a solution of H<sub>2</sub>hmc (0.25 mmol, 0.090 g) and pyridine (4 mmol, 0.080 ml) in THF (15 mL). The solution was stirred for 5 min and then filtered. After two days, pale yellow crystals of **1** were collected by filtration, washed with MeOH and dried in vacuo. Yield =62%. IR (KBr, cm<sup>-1</sup>): 3184 (br), 1648 (s), 1561 (s), 1460 (s), 1384 (s), 1264 (s), 1222 (m), 1081 (m), 1023 (m), 947 (m), 848 (w), 781 (m), 734 (m), 670 (m), 626 (w), 572 (m), 431 (m).

[Dy<sub>9</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ-OH)<sub>6</sub>(hmc<sup>2-</sup>)<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>(DMF)<sub>4</sub>](OH)·H<sub>2</sub>O·THF·DMF (**2**)

To a solution of Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.616 mmol, 0.282 g) in THF (15 mL) was added a solution of H<sub>2</sub>hmc (0.274 mmol, 0.098 g) and triethylamine (3.65 mmol, 0.268 mL) in DMF (5 mL) and THF (10 mL). The solution was stirred for 5 min at room temperature and then filtered. After one week, the crystallisation was carried out at room temperature, which yield rectangular, light yellow crystals of **2** which were collected by filtration and dried in vacuo. Yield = 17.9%. IR (KBr, cm<sup>-1</sup>): 1661 (m), 1611 (m), 1576 (m), 1514 (m), 1461 (m), 1386 (s), 1222 (d), 1082 (w), 1021 (w), 967 (s), 853 (m), 785 (w), 754 (s), 668 (w).

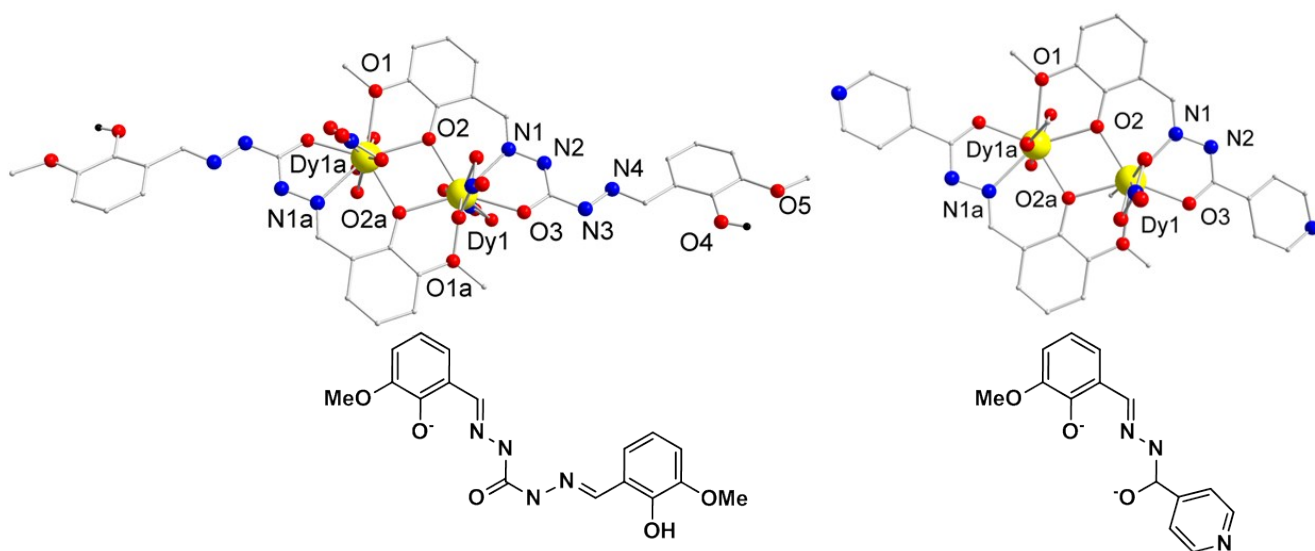
CCDC 1412245-1412246 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

### X-ray Crystallographic Studies

Single crystals of complexes **1** and **2** suitable for X-ray diffraction measurements were mounted on an Oxford Xcalibur Sapphire-3 CCD Gemini diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), and intensity data were collected with ω scans. The data collection and reduction were performed with the CrysAlisPro software,<sup>2</sup> and the absorptions were corrected by the SCALE3 ABSPACK multiscan method.<sup>3</sup> The space-group determination was based on a check of the Laue symmetry and systematic absences, and it was confirmed using the structure solution. The structure was solved and refined with the SHELXTL package.<sup>4</sup> Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. There is an additional solvent accessible void which could not be modeled for complex **2**. The program SQUEEZE<sup>5</sup> as implemented in Platon<sup>6</sup> was used to remove the contribution of the disordered solvent to the structure factors.

## Magnetic Measurement

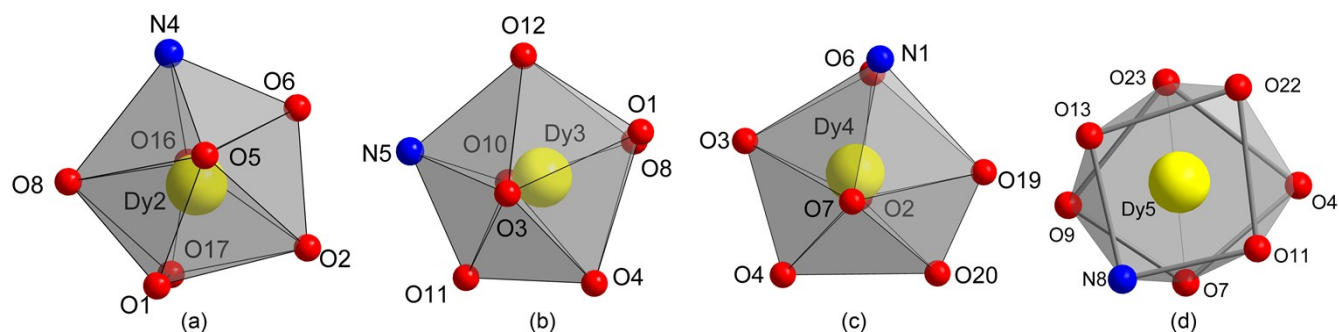
Magnetic measurements were performed using a Quantum Design SQUID magnetometer MPMS-XL7, operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T. Susceptibility measurements were performed on freshly filtered, crushed crystalline complex **1** (26.6 mg) and **2** (6.6 mg), wrapped within a polyethylene membrane. The field dependent magnetization data of complex **1** was also collected at 1.8, 3, 4, 5, 6 and 7 K under applied fields up to 5 T, and the field dependent magnetization data of complex **2** was also collected at 1.8, 3, 5, and 7 K under applied fields up to 7 T. The magnetization data were initially collected at 100 K to check for ferromagnetic impurities, found to be absent in all samples.



**Figure S1.** Top: Molecular structure of complex **1** and the dinuclear complex in the literature.<sup>1</sup> Colour code: Dy (yellow), O (red), N (blue) and C (gray). H atoms were omitted for clarity. Bottom: The deprotonated ligand of two complexes.

**Table S1.** Selected bonds (Å) and angles (°) for two dinuclear complexes.

	Complex <b>1</b>	Literature complex
Dy1-O2a	2.342(2)	2.293(7)
Dy1-O2	2.358(2)	2.362(6)
Dy1---Dy1a	3.7076(4)	3.6881(11)
Dy1-O2-Dy1a	104.14(7)	104.7(2)



**Figure S2.** Coordination polyhedral of Dy<sup>III</sup> ions geometry for Dy2 (a), Dy3 (b), Dy4 (c) and Dy5 (d) of complex **2**.

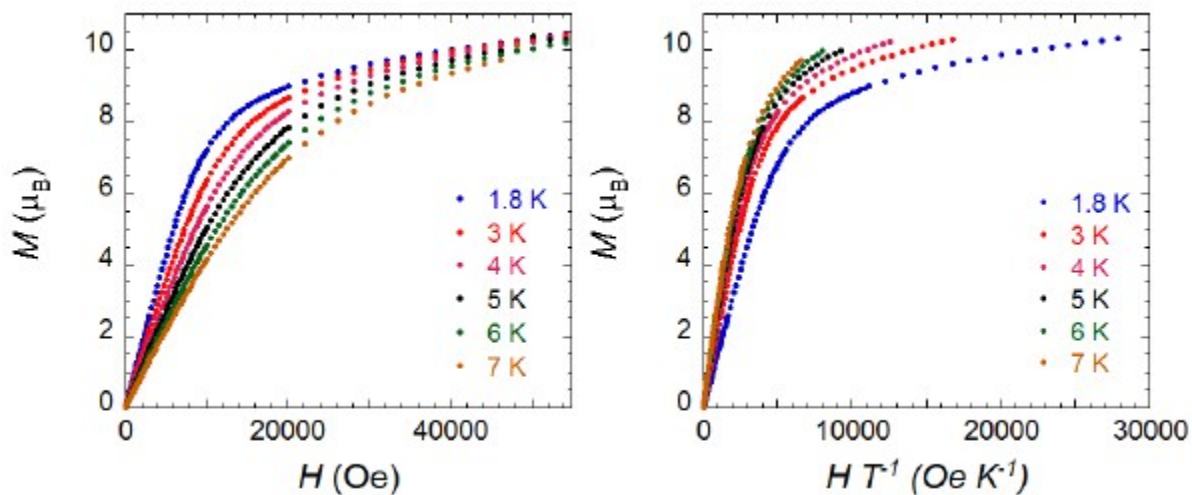


Figure S3. Field dependence of the magnetization (left) and  $M$  vs.  $HT^{-1}$  plot (right) at indicated temperatures for complex 1.

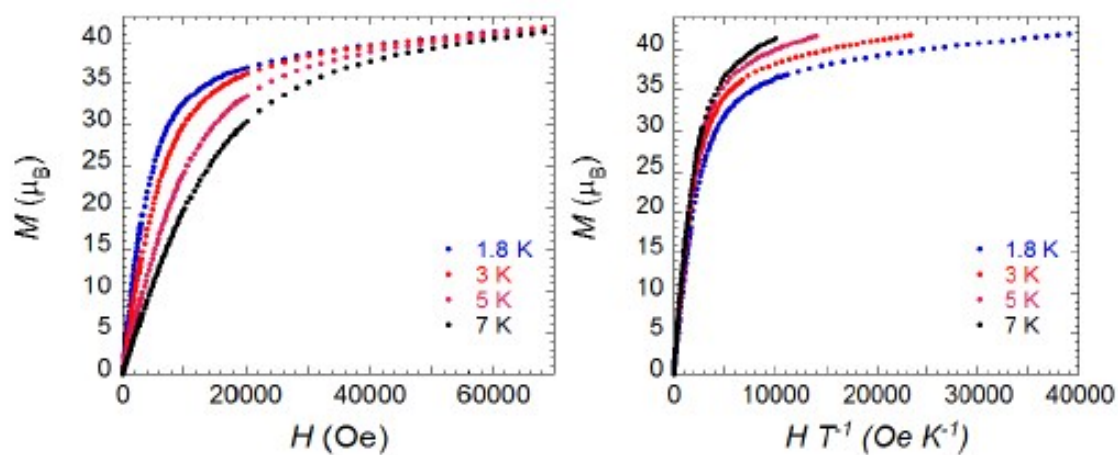


Figure S4. Field dependence of the magnetization (left) and  $M$  vs.  $HT^{-1}$  plot (right) at indicated temperatures for complex 2.

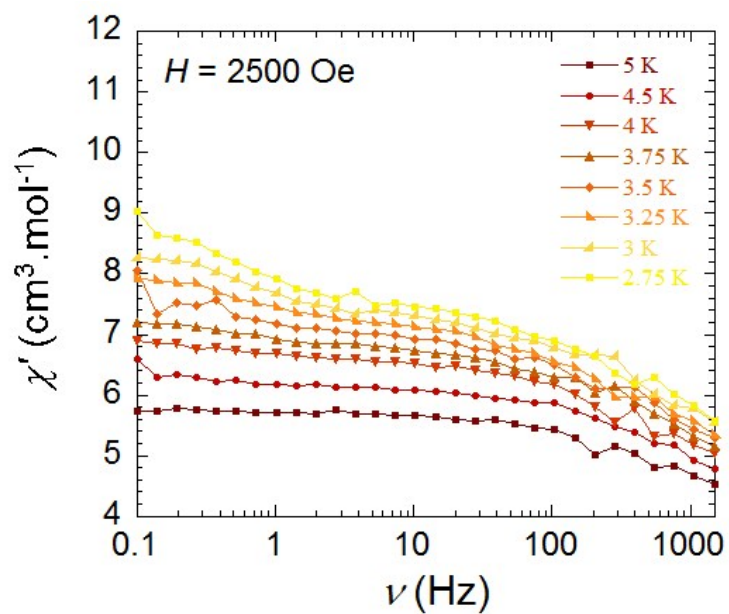


Figure S5. Frequency dependence of the in-phase ( $\chi'$ ) susceptibility of Complex 2 under 2500 Oe dc field.

## Reference

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