Supproting Information

Body-Wing Swapping in Butterfly {Fe₂Ln₂} Coordination Clusters with Triethylene Glycol as Ligand

Guo Peng,^a George E. Kostakis,^a Yanhua Lan^b and Annie K. Powell*^{a,b}

^aInstitute of Nanotechnology, Karlsruhe Institute of Technology, Hermannvon-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany, Fax: +49 721 608 48142; Tel: +49 721 60842135 E-mail: annie.powell@kit.edu;

^bInstitute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstrasse 15, 76128 Karlsruhe, Germany

X-ray Data Collection and Structure Determination. Data for **1**, **2**, **5** and **6** were collected at 180 K on a Stoe IPDS II area detector diffractometer using graphite-monochromated Mo–K α radiation. Suitable crystals were transferred directly from their mother liquor into perfluorinated polyether oil and mounted immediately on the goniometer. Semi-empirical absorption corrections were applied using *XPREP* in *SHELXTL*.¹ The structures were solved using direct methods, followed by full-matrix least-squares refinement against F^2 (all data) using *SHELXTL*.¹ Anisotropic refinement was used for all ordered non-H atoms; organic H atoms were placed in calculated positions, while coordinates of hydroxo H atoms were refined where possible (in most cases).

Synthetic part

Compound 1 FeCl₃·6H₂O (0.135 g, 0.5 mmol), Y(NO₃)₃·6H₂O (0.192 g, 0.5 mmol), pivalic acid (0.102 g, 1.0 mmol) and NaN₃ (0.067 g, 1.0 mmol) were dissolved in a mixture of triethylene glycol (10 mL) and CH₃CN (10 mL). After 30min stirring at 60 °C, NEt₃ (0.35 mL, 2.5 mmol) was added. The resulting mixture was stirred for another 3h at 60 °C and then filtered when the solution was cooled. Slow evaporation of the filtrate at room temperature gave orange crystals after 2 months. The crystals were isolated by filtration, washed with CH₃CN, and dried in air. Yield: 55mg (20%, based on Fe). Calc. (%) for $C_{32}H_{62}Y_2Fe_2N_{5.6}Cl_{0.4}O_{18}$ (Cl disorder): C 34.41, H 5.59, N 7.02; found: C 34.69, H 5.74, N 6.89. Selected IR data (cm⁻¹): 3651 (w), 3423 (br), 2959 (w), 2857 (w), 2064 (vs), 1554 (s), 1485 (m), 1421 (s), 1360 (w), 1232 (w), 1074 (s), 948 (w), 660 (w), 604 (w).

Compound 2 FeCl₃·6H₂O (0.135g, 0.5 mmol), Dy(NO₃)₃·6H₂O (0.228 g, 0.5 mmol), pivalic acid (0.102g, 1.0 mmol) and NaN₃ (0.067g, 1.0 mmol) were dissolved in a mixture of triethylene glycol (10 mL) and CH₃CN (10 mL). After 30min stirring, NEt₃ (0.35 mL, 2.5 mmol) was added. The resulting mixture was stirred for another 3h and then filtered. Slow evaporation of the filtrate at room temperature gave orange crystals after one and half months. The crystals were isolated by filtration, washed with CH₃CN, and dried in air. Yield: 75 mg (24%, based on Fe). Calc. (%) for $C_{32}H_{62}Dy_2Fe_2N_6O_{18}$: C 30.61, H 4.98, N 6.69; found: C 30.45, H 5.02, N 6.47. Selected IR data (cm⁻¹): 3647 (w), 3436 (br), 2958 (w), 2856 (w), 2062 (vs), 1552 (s), 1485 (m), 1420 (s), 1359 (w), 1231 (w), 1073 (s), 946 (w), 654 (w), 604 (w).

Compound 3 FeCl₃·6H₂O (0.135g, 0.5 mmol), Ho(NO₃)₃·6H₂O (0.230 g, 0.5 mmol), pivalic acid (0.102g, 1.0 mmol) and NaN₃ (0.067g, 1.0 mmol) were dissolved in a mixture of triethylene glycol (10 mL) and CH₃CN (10 mL). After 30min stirring at 60 °C, NEt₃ (0.42 mL, 3.0 mmol) was added. The resulting mixture was stirred for another 3h at 60 °C and then filtered when the solution was cooled. Slow evaporation of the filtrate at room temperature gave orange crystals after one week. The crystals were isolated by filtration, washed with CH₃CN, and dried in air. Yield: 198 mg (63%, based on Fe). Calc. (%) for $C_{32}H_{62}H_{02}Fe_2N_6O_{18}$: C 30.49, H 4 .96, N 6.67; found: C 30.49, H 5.04, N 6.48. Selected IR data (cm⁻¹): 3649(w), 3446 (br), 2959 (w), 2857 (w), 2063 (vs), 1553 (s), 1485 (m), 1421 (s), 1360 (w), 1232 (w), 1074 (s), 948 (w), 664 (w), 604 (w).

Compounds 4-6 Fe(NO₃)₃·6H₂O (0.202 g, 0.5 mmol) and) and pivalic acid (0.153 g, 1.5 mmol) was dissolved in a mixture of triethylene glycol (10 mL) and CH₃CN (10 mL), then NEt₃ (0.35 mL, 2.5 mmol) was added. The resulting mixture was refluxed for 1h. After cooling, a solution of Ln(NO₃)₃·6H₂O (0.192 g for **4**, 0.228 g for **5** and 0.230 g for **6**, 0.5 mmol) in 5 mL CH₃OH was added. The resulting mixture was heated under refluxed for another 2h and then then filtered when the solution was cooled. Slow evaporation of the filtrate at room temperature gave yellow crystals after 12 days for **4**, 10 days for **5** and 14 days for **6**. The crystals were isolated by filtration, washed with CH3CN, and dried in air. Yield: 16 mg for **4**, 60 mg for **5**, 70 mg for **6** (5% for **4**, 18% for **5** and 20% for **6**, based on Fe).

Calc. (%) for C₃₄H₆₆Y₂Fe₂N₂O₂₄: C 34.71, H 5.65, N 2.38; found: C 34.71, H 5.62, N 2.53. Selected IR data (cm⁻¹): 3433 (br), 2958 (w), 2889 (w), 1569 (s), 1480 (s), 1407 (s), 1370 (s), 1307 (s), 1225 (w), 1073 (s), 995 (m), 928 (m), 828 (w), 610 (w), 429(w).

Calc. (%) for C₃₄H₆₈Dy₂Fe₂N₂O₂₅: C 30.44, H 5.11, N 2.09; found: C 30.37, H 4.73, N 2.21. Selected IR data (cm⁻¹): 3435 (br), 2958 (w), 2889 (w), 1569 (s), 1479 (s), 1406 (s), 1370 (s), 1304 (s), 1224 (w), 1073 (s), 995 (m), 927 (m), 827 (w), 609 (w), 425(w).

Calc. (%) for C₃₄H₆₆Ho₂Fe₂N₂O₂₄: C 30.74, H 5.01, N 2.11; found: C 30.74, H 5.20, N 2.23. Selected IR data (cm⁻¹): 3436 (br), 2958 (w), 2889 (w), 1569 (s), 1479 (s), 1407 (s), 1369 (s), 1305 (s), 1225 (w), 1073 (s), 995 (m), 928 (m), 827 (w), 610 (w), 425(w).



Fig S1. The experimental powder XRD patterns for 3 (upper) and 4 (lower) in comparison with 1 and 6, respectively.

Table S1. Magnetic data of compounds 1-6 summarized from the dc measurements

Compounds	χT expected for non- interacting ions per complex (cm ³ Kmol ⁻¹)	χT measured at 300 K per complex (cm ³ Kmol ⁻¹)	χT measured at 1.8 K per complex (cm ³ Kmol ⁻¹)	Magnetization at 2 K and 7 T (µB)
1	8.75	8.7561	3.1917	10.035

2	37.09	37.31	14.842	20.533
3	36.89	36.639	18.078	19.901
4	8.75	8.3226	0.054227	1.1085
5	37.09	36.311	10.078	12.926
6	36.89	36.358	7.0048	13.26



Fig S2. Plots of *M vs. H* for compounds 1 - 6.



Fig S3. Plots of *M vs*. *H*/*T* for compounds **1** - **6**.

References

G. M. Sheldrick, Acta Crystallogr., Sect., A 2008, 64, 112.