Heptanuclear {Dy₂Cu₅} complex as a single-molecule magnet

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Supporting information (SI)

Physical measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded for the samples dissolved in DMSO-d_6 at 600 MHz for ^{1}H NMR and 150 MHz for ^{13}C NMR by a Varian VNMRS 600 MHz instrument. Elemental analyses were measured by Flash 2000 CHNS apparatus (Thermo Scientific). The samples for FT-IR (ATR) measurements were not dried prior to its using and were used as freshly growth crystals. FT-IR spectra were measured by ATR method in region $400 - 4000$ cm^{-1} at room temperature FT-IR spectrometer (Shimadzu IRAffinity-1) with the Quest ATR holder. Absorption spectra of H$_3$L^1 in the UV–Vis region (9000–$50\,000$ cm^{-1}) were recorded by UV–Vis–NIR spectrophotometer 50 Bio (Varian). UV-Vis spectra for solid sample (**1**) was dispersed in the Nujol oil were measured by Specord 250 Plus (Analytica Jena) with the DAD detector. Melting points were studied with thermo-microscopy by Kofler hot-stage microscope at 4°C·min^{-1} and reported without corrections.

X-ray crystal structure determination. data collection and cell refinement of suitable single crystal of **1** were made by Stoe StadiVari diffractometer using PILATUS3R 300K HPAD detector and micro-focused source Xenocs Genix3D with Cu HF at 100K. Corrections to Lorentz, polarization and multi-scan absorption effects were applied. The structure was solved by charge-flipping method and refined anisotropically by common least-squares methods. The programs ShelXT, Superflip ShelXL, OLEX2 and MERCURY have been used for structure determination, refinement and drawing.[S1-S5] The hydrogen atoms were refined with fixed distances from the parent carbon atoms. Crystal data are presented in Table S1 in detail.

Details on the synthesis/analysis

The organic reactants (2-hydroxy-1,3-propandiamine, 5-bromo-3-methoxysalicylaldehyde, 5-chloro-3-methoxysalicylaldehyde and inorganic salts (dysprosium(III) chloride hexahydrate, copper(II) nitrate trihydrate) of reagent grade were used as received. Ethanol, methanol and triethylamine were not dried and used without any further purification.

Synthesis and analytical data of H$_3$L^1. 2-hydroxy-1,3-propandiamine (1 mmol, 0.901 g) was dissolved in ethanol (15 cm^3) and 5-bromo-3-methoxysalicyl-aldehyde (2 mmol, 0.462 g) was added gradually. The resulting solution was stirred and heated under reflux for 3 h at 60° C. A yellow powder was immediately obtained, filtered and dried. Recipe was based on same manner to that describe from S.-P. Yan et al.[S6] Yield: 86 %. Melting point: 180-185 °C. *Anal Calc.* for C$_{19}$H$_{20}$Br$_2$N$_2$O$_5$ (M = 516.19 g·mol^{-1}): C, 44.21; H, 3.91; N, 5.43. Fond: C, 43.61; H, 3.89; N, 5.60. ^{1}H NMR (600 MHz, DMSO-d_6, 25 °C) δ (ppm) 13.76 (bs, OH, 2H), 8.46 (s, -CH=N-, 2H), 7.22 (d, J = 2.3 Hz, H-6', 2H), 7.08 (d, J = 2.3 Hz, H-4', 2H), 5.36 (bs, OH, 1H), 4.02-3.97 (m, H-2, 1H), 3.78 (s, OCH$_3$, 6H), 3.77 (ddd, J = 12.5, 4.2, 0.9 Hz, H-1, H-3, 2H), 3.58 (ddd, J = 12.5, 6.8, 0.7 Hz, H-1, H-3, 2H); ^{13}C NMR (150 MHz, DMSO-d_6, 25 °C) δ (ppm) 166.0 (-CH=N-), 154.0 (C-2'), 149.9 (C-3'), 124.8 (C-6'), 118.5 (C-1'), 116.8 (C-4'), 107.2 (C-5'), 68.9 (C-2), 60.9 (C-1, C-3), 56.0 (OCH$_3$). Selected IR bands: 3027(w), 3066(w), 2897(w), 2850(w), 1629(s), 1519(s), 1479(s), 1436(s), 1370(m), 1353(m), 1230(s), 1213(sh), 1092(m), 1075(m), 1016(m), 988(m), 962(m), 864(m), 835(s), 760(m), 696(m), 638(m), 578(m), 565(m), 491(sh), 420(m) (s = strong). UV/Vis (EtOH) v_{max}/10^3 cm^{-1} (c = 1.94·10^{-5} mol·dm^3): 23.50 (0.097; ε = 5007 M^{-1}·cm^{-1}); 29.28 (0.084; ε = 4336 M^{-1}·cm^{-1}); 34.02 (0.182; ε = 9395 M^{-1}·cm^{-1}); 43.53 (0.920; ε = 47489 M^{-1}·cm^{-1}).

Synthesis and analytical data of [(H$_2$O)$_6$Dy^{III}(μ$_2$-L^1)$_2$(μ$_3$-O)$_4$Cu^{II}$_5$(μ$_2$-Cl)$_2$], 1. H$_3$L^1 (1 mmol, 0.179 g) was dissolved in methanol (15 cm^3) and triethylamine was added (2 mmol 140 cm^3). The solution was stirred for 20 min, while in the second beaker, copper(II) nitrate trihydrate (1 mmol, 0.121 g) was dissolved in methanol (9.2 cm^3). Finally, the two solutions were combined and stirred for 20 min before dysprosium(III) chloride hexahydrate was added. The resulting mixture was stirred at room temperature for two hours, filtered and allowed to crystallize. Green crystals were collected after 5 days. Yield: 2.1%. Melting point: > 300°C. *Anal Calc.* for C$_{38}$H$_{46}$Br$_4$Cl$_2$Cu$_5$Dy$_2$N$_4$O$_{20}$ (M = 1912.03 g·mol^{-1}): C, 23.87; H, 2.42; N, 2.93. Found: C, 22.87; H, 3.53; N, 3.89. UV/Vis (Nujol) v_{max}/10^3 cm^{-1} (relat. absorb.): 15.39 (0.257); 27.58 (0.748); 35.96 (0.874).

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S1 G. M. Sheldrick, *Acta Crystallogr*, 2015, **A71**, 3

S2 L. Palatinus, G. Chapuis, *J. Appl. Cryst*, 2007, **40**, 786.

S3 G.M. Sheldrick. *Acta Crystallogr*, 2015, **C71**, 3.

S4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst*, 2009, **42**, 339.

S5 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L., Rodriguez-Monge, R. Taylor, J. V.D. Streek, P. A. Wood*, J. App. Crystallogr*, 2008, **41**, 466.

S6 L. Jiang, D.-Y. Zhang, J.-J. Suo, W. Gu, J.-L. Tian, X. Liu, S.-P. Yan, *Dalton Trans.*, 2016, **45**, 10233

Quantum-chemical calculations. Density functional theory (DFT) calculations were performed with ORCA 5.0.4 computational package at the experimental geometry of complex **1** established by the X-ray diffraction [S7]. However, the structure was truncated as needed or otherwise modified to make the calculations more efficient. The relativistic effects were included in the calculations with the second-order Douglas-Kroll-Hess (DKH) approximation [S8]. All calculations included SARC-DKH-TZVP (for Dy) and DKH-def2-TZVP (for for all other elements) basis sets and utilized the RIJCOSX approximation with the AutoAux generation procedure [S9]. Increased integration grids (DefGrid2, for Dy the SpecialGrid option was set to 8) and tight SCF convergence criteria were also used. Calculation of the electronic structure and the exchange coupling constant *J* were based on B3LYP functional [S10]. The *J* values have been calculated using the broken-symmetry solution for low-spin wave function [S11]. The time-dependent DFT method was used to model the electronic spectra of individual metal centers using the ωB97X-D3 functional [S12].

[S7] (a) F. Neese, (2012) The ORCA program system, Wiley Interdiscip. Rev.: *Comput. Mol. Sci.*, **2**, 73. (b) Neese, F. (2017) Software update: the ORCA program system, version 4.0, Wiley Interdiscip. Rev.: *Comput. Mol. Sci.*, **8**, e1327. (c) F. Neese, F. Wennmohs, U. Becker, C. Riplinger, (2020) The ORCA quantum chemistry program package, *J. Chem. Phys.*, **152**, 224108.

[S8] M. Reiher, Douglas–Kroll–Hess Theory: a relativistic electrons-only theory for chemistry. *Theor. Chem. Acc.*, 2006, **116**, 241.

[S9] G. L. Stoychev, A. A. Auer, F. Neese, *J. Chem. Theory Comput.*, 2017, **13**, 554.

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[S11] (a) G. David, F. Wennmohs, F. Neese, N. Ferre, *Inorg. Chem.*, 2018, **57**, 12769. (b) D. A. Pantazis, V. Krewald, M. Orio, F. Neese, *Dalton Trans.*, 2010, **39**, 4959.

[S12] T. Risthaus, A. Hansen, S. Grimme, *Phys. Chem. Chem. Phys.*, 2014, **16**, 14408 .

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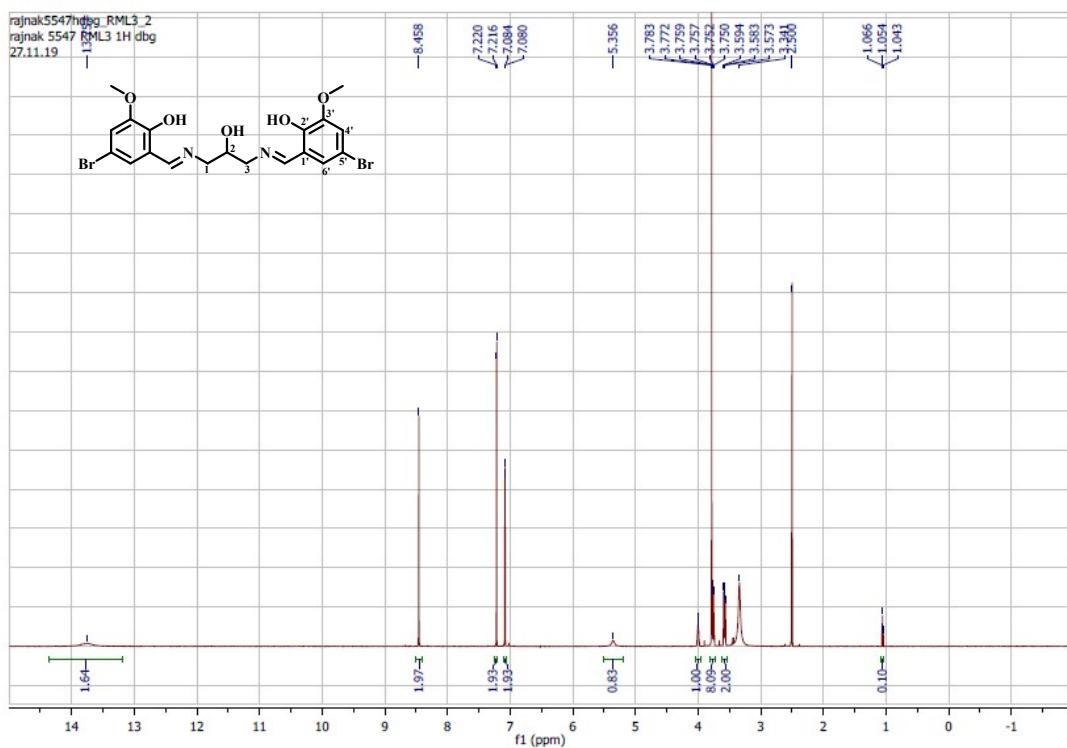
Fig. S1. ^{1}H NMR spectrum of ligand **H₃L¹**.
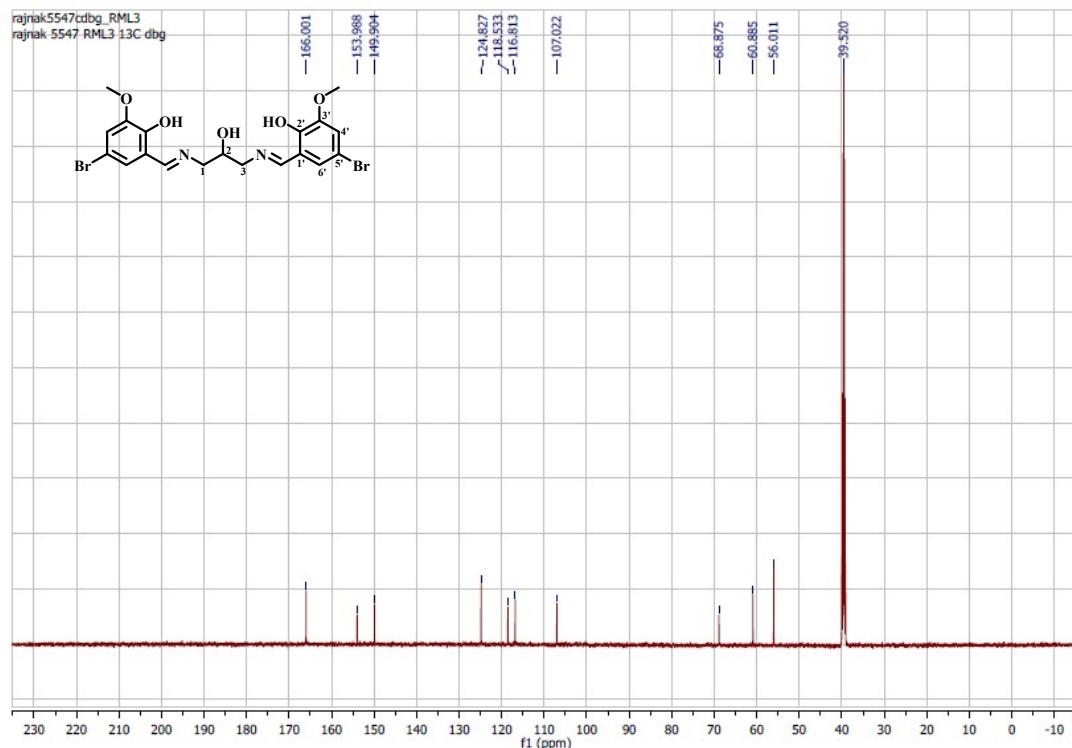
Fig. S2. ^{13}C NMR spectrum of ligand **H₃L¹**.

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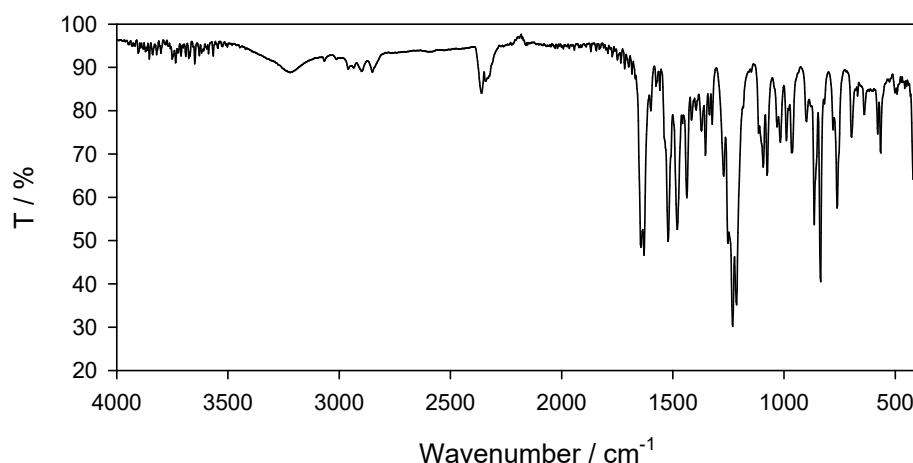
Fig. S3. FT-IR (ATR) spectrum of **H₃L¹**.
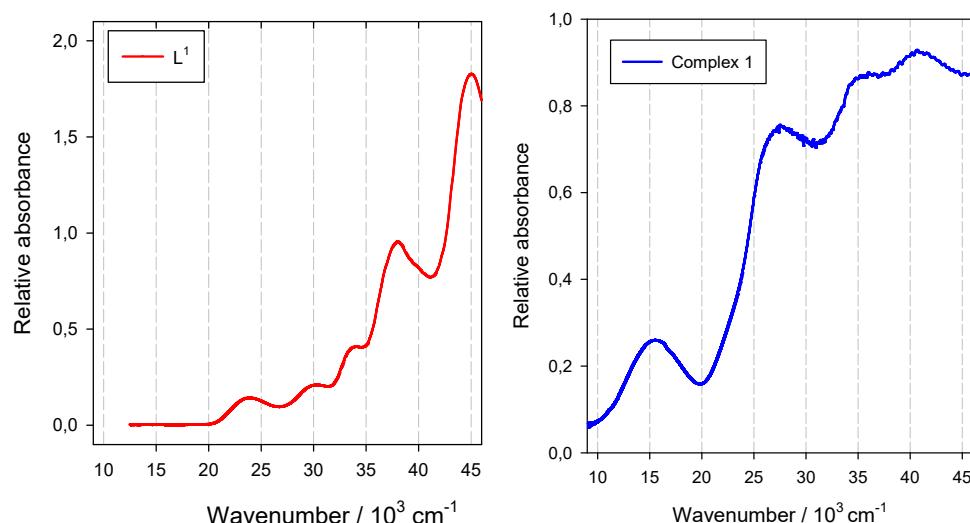
Fig. S4. Electronic spectra of **H₃L¹** (in EtOH, c = 1.94 x 10⁻⁵ g·mol⁻¹) and **1** (Nujol suspension).
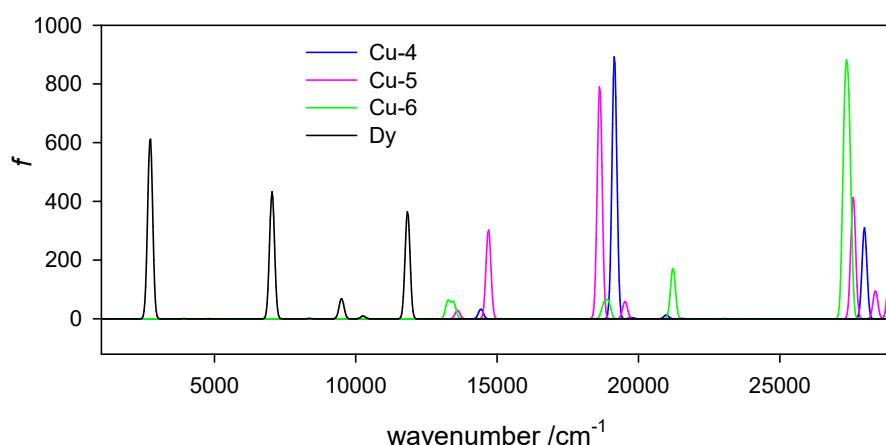
Fig. S5. Calculated (TD-DFT) electronic spectra for individual metal centres (four-, five- and six-coordinated Cu(II) and Dy(III)) in the complex **1**.

Heptanuclear {Dy$_2$Cu$_5$} complex as a single-molecule magnet

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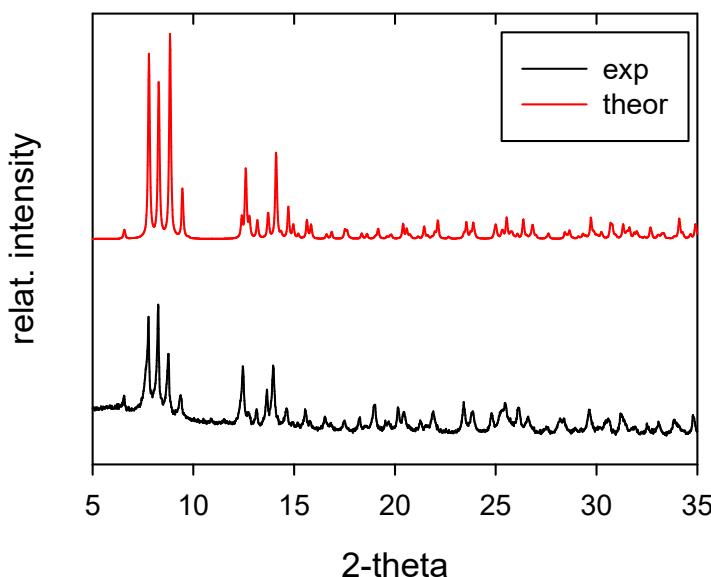
**Fig. S6** Calculated powder diffraction pattern for **1** from cif-file (theor), and recorded pattern at Cu λ = 1.54060 Å (exp).

Table S1. Crystal data and structure refinement for **1**.

	Complex 1
Empirical formula	$C_{38}H_{46}Br_4Cl_2Cu_5Dy_2N_4O_{20}$
Formula weight /g mol^{-1}	1912.03
Crystal system	triclinic
Space group	P-1
Temperature /K	150
Crystal size /mm	$0.18 \times 0.15 \times 0.12$
Z	1
a / Å	10.7667(2)
b / Å	12.5061(3)
c / Å	15.2672(3)
α /°	66.153(2)
β /°	69.597(2)
γ /°	74.811(2)
V /Å^3	1744.60(7)
ρ_{calc} /g cm^{-3}	1.820
μ /mm^{-1}	16.775
F(000)	913.0
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	6.584 to 144.7
Index ranges	$-13 \leq h \leq 12, -12 \leq k \leq 15, -18 \leq l \leq 16$
Data/restraints/parameters	6663/0/345
Goodness-of-fit on F^2	1.111
Final R indexes [I>=2σ (I)]	R_1 = 0.0496, wR_2 = 0.1371
R indices (all data)	R_1 = 0.0594, wR_2 = 0.1430
Colour	Dark green
CCDC code	2160393

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Table S2. Selected bond lengths (Å) in **1**.

Dy1-Cu1	3.4989(4)	Cu1-O6	1.969(4)
Dy1-Cu2	3.4113(10)	Cu1-O6[1]	1.969(4)
Dy1-Cu3[1]	3.4844(10)	Cu1-O7	1.950(5)
Dy1-O1	2.601(5)	Cu1-O7[1]	1.950(5)
Dy1-O2	2.336(4)	Cu1-Cl1[1]	2.7889(17)
Dy1-O4[1]	2.357(5)	Cu1-Cl1	2.7889(17)
Dy1-O5[1]	2.544(5)	Cu2-O2	1.959(5)
Dy1-O6	2.397(5)	Cu2-O3	1.960(5)
Dy1-O7[1]	2.462(5)	Cu2-O6	1.950(4)
Dy1-O8	2.376(4)	Cu2-N1	1.917(6)
Dy1-O9	2.380(6)	Cu2-Cl1[1]	2.6738(19)
Dy1-O10	2.400(5)	Cu3-O3	1.950(5)
		Cu3-O4	1.954(5)
		Cu3-O7	1.970(4)
		Cu3-N2	1.918(6)

Atom numbering:
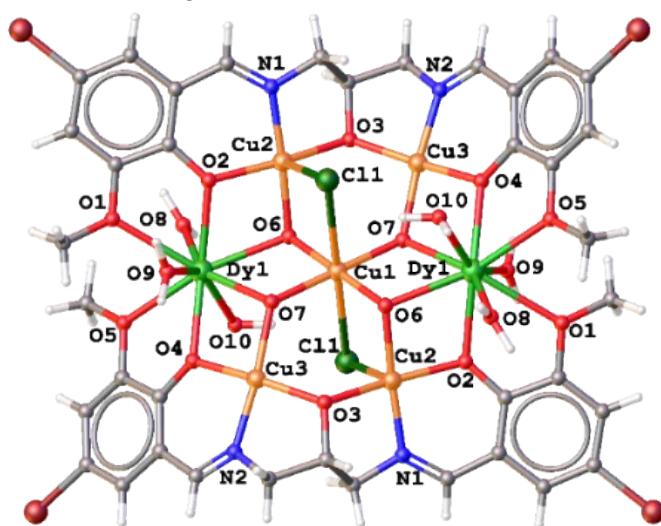
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Table S3. Selected bond angles (°) in chromophores of **1**.

|					
Cu2-Dy1-Cu1	54.448(18)	O2-Dy1-O4^1	150.70(18)	O4^1-Dy1-O1	111.29(17)
Cu2-Dy1-Cu3^1	112.34(3)	O2-Dy1-O5^1	130.11(16)	O4^1-Dy1-O5^1	63.82(15)
Cu3^1-Dy1-Cu1	59.884(18)	O2-Dy1-O6	67.59(16)	O4^1-Dy1-O6	118.62(16)
O1-Dy1-Cu1	142.94(11)	O2-Dy1-O7^1	96.33(15)	O4^1-Dy1-O7^1	65.44(15)
O1-Dy1-Cu2	96.04(11)	O2-Dy1-O8	74.53(16)	O4^1-Dy1-O8	133.48(17)
O1-Dy1-Cu3^1	131.21(12)	O2-Dy1-O9^1	80.1(2)	O4^1-Dy1-O9	72.4(2)
O2-Dy1-Cu1	82.52(12)	O2-Dy1-O10	132.95(18)	O4^1-Dy1-O10	73.19(19)
O2-Dy1-Cu2	33.72(12)	O4^1-Dy1-Cu1	91.03(12)	O5^1-Dy1-Cu1	146.70(12)
O2-Dy1-Cu3^1	127.79(11)	O4^1-Dy1-Cu2	144.63(11)	O5^1-Dy1-Cu2	150.41(11)
O2-Dy1-O1	63.39(16)	O4^1-Dy1-Cu3^1	32.32(11)	O5^1-Dy1-Cu3^1	95.88(11)
O5^1-Dy1-O1	69.91(16)	O10-Dy1-Cu1	80.66(13)	Cl1-Cu1-Dy1	87.02(4)
O6-Dy1-Cu1	32.73(10)	O10-Dy1-Cu2	104.54(13)	Cl1^1-Cu1-Dy1^1	87.02(4)
O6-Dy1-Cu2	33.87(11)	O10-Dy1-Cu3^1	78.31(12)	Cl1-Cu1-Dy1^1	92.98(4)
O6-Dy1-Cu3^1	90.69(10)	O10-Dy1-O1	133.05(17)	Cl1^1-Cu1-Cl1^1	180.0
O6-Dy1-O1	128.79(15)	O10-Dy1-O5^1	71.64(18)	O2-Cu2-Dy1	41.45(13)
O6-Dy1-O5^1	143.60(17)	O10-Dy1-O7^1	92.55(17)	O2-Cu2-O3	167.85(19)
O6-Dy1-O7^1	65.31(16)	Dy1^1-Cu1-Dy1	180.0	O2-Cu2-Cl1^1	98.17(15)
O6-Dy1-O10	74.78(17)	O6^1-Cu1-Dy1	138.85(14)	O3-Cu2-Dy1	136.87(14)
O7^1-Dy1-Cu1	32.69(11)	O6-Cu1-Dy1^1	138.85(14)	O3-Cu2-Cl1^1	93.98(14)
O7^1-Dy1-Cu2	79.60(11)	O6-Cu1-Dy1	41.15(14)	O6-Cu2-Dy1	43.22(14)
O7^1-Dy1-Cu3^1	33.42(10)	O6^1-Cu1-Dy1^1	41.15(4)	O6-Cu2-O2	84.67(19)
O7^1-Dy1-O1	132.94(17)	O6^1-Cu1-O6	180.0	O6-Cu2-O3	95.1(2)
O7^1-Dy1-O5^1	129.23(15)	O6^1-Cu1-Cl1	87.93(13)	O6-Cu2-Cl1^1	91.67(14)
O8-Dy1-Cu1	112.98(12)	O6^1-Cu1-Cl1^1	92.07(13)	N1-Cu2-Dy1	134.4(2)
O8-Dy1-Cu2	74.80(12)	O6-Cu1-Cl1^1	87.93(13)	N1-Cu2-O2	93.3(2)
O8-Dy1-Cu3^1	150.70(12)	O6-Cu1-Cl1	92.07(13)	N1-Cu2-O3	85.7(2)
O8-Dy1-O1	73.11(17)	O7-Cu1-Dy1^1	42.99(13)	N1-Cu2-O6	173.9(2)
O8-Dy1-O5^1	76.18(16)	O7^1-Cu1-Dy1	42.99(13)	N1-Cu2-Cl1^1	94.34(18)
O8-Dy1-O6	80.70(16)	O7^1-Cu1-Dy1^1	137.01(13)	Cl1^1-Cu2-Dy1	97.08(5)
O8-Dy1-O7^1	145.56(17)	O7-Cu1-Dy1	137.01(13)	O3-Cu3-Dy1^1	140.14(14)
O8-Dy1-O9	137.0(2)	O7-Cu1-O6	96.01(19)	O3-Cu3-O4	169.6(2)
O8-Dy1-O10	72.40(17)	O7^1-Cu1-O6	83.99(19)	O3-Cu3-O7	99.32(19)
O9-Dy1-Cu1	97.19(18)	O7-Cu1-O6^1	83.99(19)	O4-Cu3- Dy1^1	40.16(13)
O9-Dy1-Cu2	101.8(2)	O7^1-Cu1-O6^1	96.01(19)	O4-Cu3-O7	83.25(19)
O9-Dy1-Cu3^1	71.15(16)	O7^1-Cu1-O7	180.0	O7-Cu3- Dy1^1	43.50(13)
O9-Dy1-O1	64.5(2)	O7^1-Cu1-Cl1^1	92.43(14)	N2-Cu3- Dy1^1	132.61(17)
O9-Dy1-O5^1	95.4(2)	O7-Cu1-Cl1	92.43(14)	N2-Cu3-O3	85.5(2)
O9-Dy1-O6	120.5(2)	O7^1-Cu1-Cl1^1	87.57(14)	N2-Cu3-O4	92.5(2)
O9-Dy1-O7^1	70.6(2)	O7-Cu1-Cl1^1	87.57(14)	N2-Cu3-O7	174.3(2)
O9-Dy1-O10	145.4(2)	Cl1^1-Cu1-Dy1	92.98(4)		

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Table S4. Comparison of Dy₂Cu₅ complexes.

1, Dy: 9-coordination, Cu: 4-, 5-, 6-coordination	2, Dy: 9-coordination, Cu: 4-, 5-, 6-coordination
CCDC: 2160393 DC: $M_{mol}/N_A = 14.2$ μ_B at $T = 2.0$ & $B = 7$ T, no saturation; $\chi T/C_0 = 69.4$ at $T = 300$ K; χ & M –fitted AC: Two (three) relaxation modes, HF: $U_{eff}/k_B = 25$ K, $\tau_0 = 1.1 \times 10^{-7}$ s, $B_{DC} = 0.2$ T. This work (**1**), $L^1 = L^{Br}$	CCDC: 2194405 Unpublished complex from C. Rajnak's group, $L^2 = L^{Cl}$
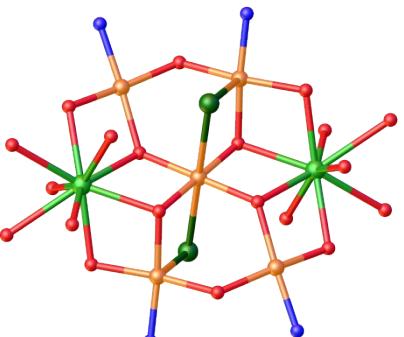
Dy: 8-coordination, Cu: 5-, 6-coordination	Dy: 8-coordination, Cu: 4-, 5-coordination
CCDC: CONZIQ DC: χ – not fitted; M – plotted, not digitized. AC: single mode relaxation (HF), on-set of LF – ignored, $U_{eff}/k_B = 4$ K, $\tau_0 = 3 \times 10^{-6}$ s; $B_{DC} = 0.09$ T V. Chandrasekhar, A. Dey, S. Das, M. Rouxieres, R. Clerac, *Inorg.Chem.* (2013), **52**, 2588. https://doi.org/10.1021/ic302614k	CCDC: GASJUI DC: χ – not fitted; M – plotted, not digitized. AC: silent χ" Lin Jiang, Bin Liu, Hao-Wen Zhao, Jin-Lei Tian, Xin Liu, Shi-Ping Yan, *CrystEngComm* (2017), **19**, 1816. https://doi.org/10.1039/C6CE02519F
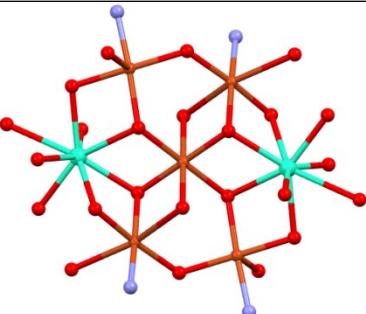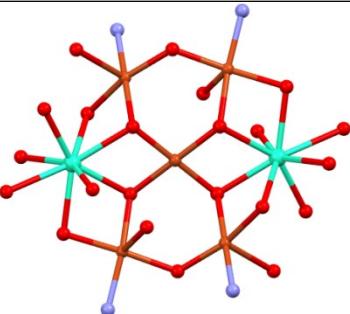
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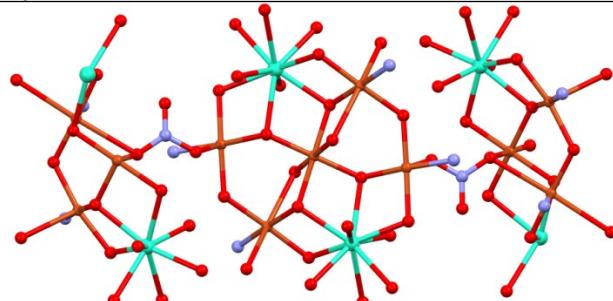
Dy: 8-coordination, Cu: 5-, 6-coordination	Dy: 9-coordination, Cu: 5-, 6-coordination
CCDC: KELFIT. catena network via NO₃, DC: χ – not fitted; M – plotted, not digitized. AC: U_{eff}/k_B = 8 K, τ_0 = 3.1 × 10⁻⁶ s; B_{DC} = 0 A. Dey, S. Das, S. Kundu, A. Mondal, M. Rouzieres, C. Mathoniere, R. Clerac, R.S. Narayanan, V. Chandrasekhar, *Inorg.Chem.* (2017), **56**, 14612. https://doi.org/10.1021/acs.inorgchem.7b02450	CCDC: NEYCUS, catena network via NO₃, DC: χ – not fitted; M – plotted, not digitized. AC (estimate, no fitting): U_{eff}/k_B =12 K, τ_0 = 10⁻⁶ s; B_{DC} = 0 A. Dey, S. Das, M.A. Palacios, E. Colacio, V. Chandrasekhar, *Eur.J.Inorg.Chem.* (2018), 1645. https://doi.org/10.1002/ejic.201701429
Dy: 9-coordination, Cu: 4-, 5-, 6-coordination	
CCDC: SODQEK DC: M_{mol}/N_A = 21.3 μ_B at T = 2.0 & B = 5 T, no saturation, χ – not fitted; AC: single mode relaxation, U_{eff}/k_B =13 K, τ_0 = 1.2 × 10⁻⁶ s; B_{DC} = 0; D. Dermitzaki, V. Psycharis, Y. Sanakis, Th. C. Stamatatos, M. Pissas, C. P. Raptopoulou, *Polyhedron*, 2019, **169**, 135-143. https://doi.org/10.1016/j.poly.2019.05.004	
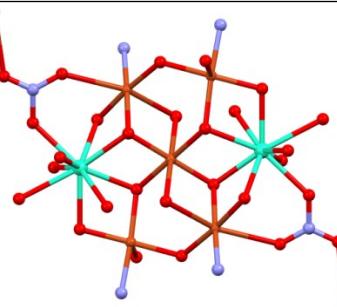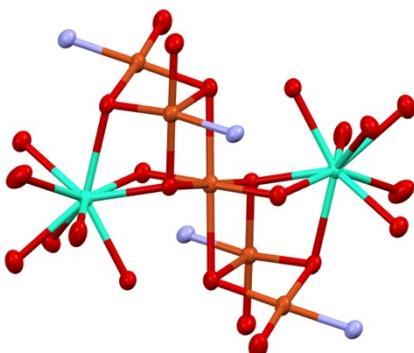
Table S5. Coordination polyhedra in **1**.

Atom	N_k	Chromophore	Shape index	Geometry	Abbr.
Cu1	6	{CuO₄Cl₂}	3.179	Octahedron	Oh
Cu2	5	{CuO₃NCl}	1.146	Square pyramid	Spy
Cu2¹	5	{CuO₃NCl}	1.146	Square pyramid	Spy
Cu3	4	{CuO₃N}	0.699	Square	Sq
Cu3¹	4	{CuO₃N}	0.699	Square	Sq
Dy1	9	{DyO₉}	7.048	Capped cube	Ccu
Dy1¹	9	{DyO₉}	7.053	Capped cube	Ccu

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DFT calculations

MO381: E = -5.86 eV	MO382: E = -5.79 eV	MO383: E = -5.63 eV
MO384: E = -5.55 eV	MO385: E = -5.43 eV	MO386: E = -5.42 eV
MO387: E = -5.35 eV	MO388: E = -5.32 eV	MO389: E = -5.30 eV
MO390: E = -4.98 eV	MO391: E = -2.67 eV	MO392: E = -2.54 eV
MO393: E = -2.49 eV	MO394: E = -2.46 eV	MO395: E = -1.42 eV
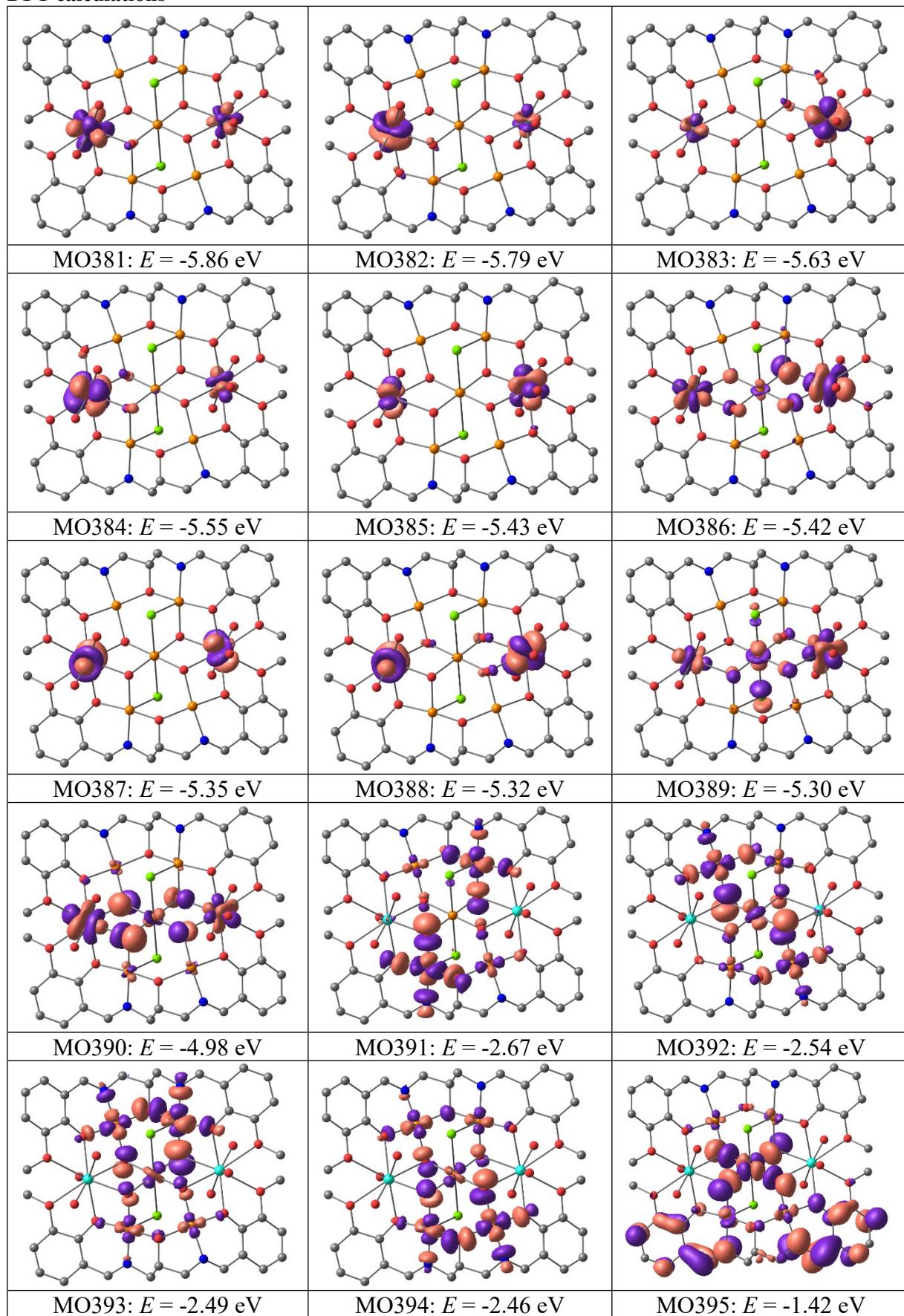
Fig. S7. Single-occupied quasi-restricted orbitals (DFT) for **1**.

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DC magnetic data

Factoring of large-dimensional matrices according to the spin S and/or total angular momentum J

The principal problem associated with a computational approach for large exchange coupled systems lies in the size of the interaction matrices. The Heisenberg Hamiltonian appropriate to the exchange coupled system reads

$$\hat{H}^{\text{ex}} = -\sum_{A<B}^{N} J_{AB}(\mathbf{S}_A \cdot \mathbf{S}_B)$$

and it generates an interaction matrix $H_{LK} = \left\langle L \middle| \hat{H}^{\text{ex}} \middle| K \right\rangle$ in the basis set of spin kets. The size of such a matrix grows rapidly with the number of constituent spins, i.e.

$$M = \prod_{A=1}^{N}(2S_A + 1)$$

In the {Dy$_2$Cu$_5$} system with J(Dy) = 15/2 and S(Cu) = 1/2 the total number of basis set functions is $N = 16^2 \cdot 2^5$ = 8192. Such a big interaction matrix can be factored, using the apparatus of the irreducible tensor operators, according to the molecular J = 1/2 through 35/2 to smaller matrices of the dimension 20, 30, 32, 32, 32, 32, 32, 32, 32, 32, 32, 32, 32, 31, 26, 16, 6 and 1. In this model the molecular J is a "good quantum number" and the Zeeman term need be applied assuming uniform g-factors, g_{eff}.

    The Heisenberg exchange Hamiltonian commutes with the total spin of the system

$$\left[\hat{H}^{\text{ex}}, \hat{S}^2\right] = 0 , \quad \left[\hat{H}^{\text{ex}}, \hat{S}_z\right] = 0$$

Therefore a set of eigenstates common for $\{\hat{H}^{\text{ex}}, \hat{S}^2, \hat{S}_z\}$ operators exists; this means that the states spanning different total spin (or J) are orthogonal

$$H_{LK} = \left\langle L:...S'M' \middle| \hat{H}^{\text{ex}} \middle| K:...SM \right\rangle = \delta_{S'S}\delta_{M'M}(2S+1)^{-1/2}\left\langle L:...S \middle\| \hat{H}^{\text{ex}} \middle\| K:...S \right\rangle$$

It allows a factoring of the interaction matrix into blocks of a much lower size

$$\mathbf{H}^{\text{ex}} \rightarrow \begin{pmatrix} \boxed{S = S_{\min}} & 0 & ... & 0 & 0 \\ 0 & \boxed{S = S_{\min}+1} & ... & 0 & 0 \\ ... & ... & ... & ... & ... \\ 0 & 0 & ... & \boxed{S = S_{\max}-1} & 0 \\ 0 & 0 & ... & 0 & \boxed{S = S_{\max}} \end{pmatrix}$$

which can be treated (diagonalized) independently.

    The matrix elements of the interaction operators in the coupled basis set of spin kets $\left|K\right\rangle = \left|(S_1, S_2, ...S_N), (S_{12}, S_{1...3}, ..., S_{1...N}), S\right\rangle$ have been generated with the help of the irreducible tensor operators for a loop for $S = S_{\min}$ until $S = S_{\max}$. The intermediate spins (IS) are abbreviated as $S_{1...N} = \overset{\%}{S}_N$ and the full set of IS is $(\overset{\%}{S}_N)$. The general form of such matrix elements utilizes a consecutive decoupling of spins until the elementary spin operators with the help of the 9j-symbols (recoupling coefficients of the angular momenta) according to the formula

$$\left\langle S_1 S_2 ...S_N(\overset{\%}{S})S' \middle\| \hat{H}^{\text{ex}} \middle\| S_1 S_2 ...S_N(\overset{\%}{S})S \right\rangle$$

$$= \sum_{k_1 k_2 ...k_N} \left\langle S_N \middle\| \hat{T}_{k_N}(\overset{r}{S}_N) \middle\| S_N \right\rangle \times \sum_{k_2' k_3' ...k_{N-1}'} G[k_1 k_2 (\overset{\%}{k}_2)k_3 (\overset{\%}{k}_3)...k_{N-1}(\overset{\%}{k}_{N-1})k_N]$$

$$\times \prod_{i=1}^{N-1}[(2\overset{\%}{S}_{i+1}+1)(2\overset{\%}{S}_{i+1}+1)(2\overset{\%}{k}_{i+1}+1)]^{1/2} \begin{Bmatrix} \overset{\%}{S}_i & \overset{\%}{S}_i & \overset{\%}{k}_i \\ S_{i+1} & S_{i+1} & k_{i+1} \\ \overset{\%}{S}_{i+1} & \overset{\%}{S}_{i+1} & \overset{\%}{k}_{i+1} \end{Bmatrix} \left\langle S_i \middle\| \hat{T}_{k_i}(\overset{r}{S}_i) \middle\| S_i \right\rangle$$

The only non-zero proportionality factor accounting for the relationship between the scalar and tensor product of spin operators is

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$$G[k_1 k_2 (\tilde{k}_2) k_3 (\tilde{k}_3)...k_{N-1}(\tilde{k}_{N-1})k_N] = \sqrt{3} J_{ij}$$

where the tensor ranks are $k_i = k_j = 1$ for $i \neq j$, $k_f = 0$ for $f \neq i,j$, and $k = \tilde{k}_N = 0$. The matrix elements of the elementary spin operators are trivial

$$\left\langle S_f \left\| \hat{T}_{k_f=0}(\vec{S}_f) \right\| S_f \right\rangle = (2s_f + 1)^{1/2}$$

$$\left\langle S_f \left\| \hat{T}_{k_f=1}(\vec{S}_f) \right\| S_f \right\rangle = [s_f(s_f + 1)(2s_f + 1)]^{1/2}$$

with $(s_f) = S_1 S_2 ... S_N$.

A computational problem arises when the magnetic field is applied: the matrix elements of the Zeeman term in the basis set of the coupled kets <u>are off-diagonal</u> in the total spin number. There is one exception: when all g-factors are equal, then the off-diagonal matrix elements of the Zeeman operator vanish exactly. This is really a fortunate case, since then the Zeeman contributions can be simply added to the roots of the zero-field Hamiltonian

$$\varepsilon(S,B) = \varepsilon_0(S) + \mu_B g_{iso} B M_S$$

Then the magnetic functions (magnetization and susceptibility) can be <u>exactly</u> expressed with the help of the thermodynamic partition function

$$M_{mol} = N_A \frac{1}{Z} T_1$$

$$\chi_{mol} = \frac{N_A \mu_0}{k_B T} \frac{1}{Z^2} (T_2 Z - T_1^2)$$

The terms entering the magnetization and the differential magnetic susceptibility are

$$Z = \sum_i \exp(-\varepsilon_i / k_B T) = \sum_{S=S_{min}}^{S_{max}} \sum_{M_S=-S}^{+S} \exp[(n_S J - \mu_B g B M_S) / k_B T]$$

$$T_1 = \sum_i \left(-\frac{\partial \varepsilon_i}{\partial B} \right) \exp(-\varepsilon_i / k_B T) = \mu_B g \sum_{S=S_{min}}^{S_{max}} \sum_{M_S=-S}^{+S} M_S \exp[(n_S J - \mu_B g B M_S) / k_B T]$$

$$T_2 = \sum_i \left(\frac{\partial \varepsilon_i}{\partial B} \right)^2 \exp(-\varepsilon_i / k_B T) = (\mu_B g)^2 \sum_{S=S_{min}}^{S_{max}} \sum_{M_S=-S}^{+S} M_S^2 \exp[(n_S J - \mu_B g B M_S) / k_B T]$$

with $n_S = S(S+1)/2$.

The critical step of the procedure is the evaluation of the reduced matrix elements of the compound operator

$$R_{I'S';IS}^{AB(k)} = \left\langle I'S' \left\| \hat{T}_k (\vec{S}_A \otimes \vec{S}_B) \right\| IS \right\rangle$$

which depends upon all intermediate spins $(I'S';IS)$; then the decoupling formula over the uncoupled spins adopts a form

$$\left\langle S_1 S_2 ... S_N; \tilde{S}_2 \tilde{S}_3 ... \tilde{S}_{N-1} S' \left\| \hat{T}_k \right\| S_1 S_2 ... S_N; \tilde{S}_2 \tilde{S}_3 ... \tilde{S}_{N-1} S \right\rangle = \left\langle S_1 \left\| \hat{T}_{k1}(\vec{S}_1) \right\| S_1 \right\rangle$$

$$\times [(2\tilde{S}_2'+1)(2\tilde{S}_2+1)(2\tilde{k}_2+1)]^{1/2} \begin{Bmatrix} S_1 & S_1 & k_1 \\ S_2 & S_2 & k_2 \\ \tilde{S}_2' & \tilde{S}_2 & \tilde{k}_2 \end{Bmatrix} \left\langle S_2 \left\| \hat{T}_{k2}(\vec{S}_2) \right\| S_2 \right\rangle$$

$$\times [(2\tilde{S}_3'+1)(2\tilde{S}_3+1)(2\tilde{k}_3+1)]^{1/2} \begin{Bmatrix} \tilde{S}_2' & \tilde{S}_2 & \tilde{k}_2 \\ S_3 & S_3 & k_3 \\ \tilde{S}_3' & \tilde{S}_3 & \tilde{k}_3 \end{Bmatrix} \left\langle S_3 \left\| \hat{T}_{k3}(\vec{S}_3) \right\| S_3 \right\rangle$$

$$\times [...]...\times [(2S'+1)(2S+1)(2k+1)]^{1/2} \begin{Bmatrix} \tilde{S}_{N-1}' & \tilde{S}_{N-1} & \tilde{k}_{N-1} \\ S_N & S_N & k_N \\ S' & S & k \end{Bmatrix} \left\langle S_N \left\| \hat{T}_{kN}(\vec{S}_N) \right\| S_N \right\rangle$$

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where $\overset{o}{S_i} = S_{12\ldots i}$ denote the intermediate spins and $\overset{o}{k_i} = k_{12\ldots i}$ the intermediate operator ranks.

In the above procedure two kinds of the operators are met

a) bilinear isotropic exchange

$$\hat{H}^{\text{iso}} = \sum_A^N \sum_{B>A}^N (-J_{AB})(\vec{S}_A \cdot \vec{S}_B)\hbar^{-2} = \sum_A^N \sum_{B>A}^N (-J_{AB})(-\sqrt{3})\left\{\hat{T}_{0,0}(\vec{S}_A \otimes \vec{S}_B)\right\}\hbar^{-2}$$

b) the Zeeman operator

$$\hat{H}^Z = \mu_B \sum_A^N (\vec{B} \cdot \bar{\bar{g}}_A \cdot \vec{S}_A)\hbar^{-1} = \mu_B \sum_A^N \sum_{q=-1}^{+1} (-1)^q (\vec{B} \cdot \bar{\bar{g}}_A)_{1,-q} \left\{\hat{T}_{1,q}(\vec{S}_A)\right\}\hbar^{-1}$$

For details see: R. Boča, A Handbook of Magnetochemical Formulae, Elsevier, Amsterdam, 2012.

Table S6. Topological matrix for exchange interactions referring to the core of **1**.

	Dy	Cu4	Cu5	Cu6	Cu5'	Cu4'	Dy'
Dy	-	J1	J2	J3	-	-	-
Cu4		-	J4	J5	-	-	-
Cu5			-	J6	-	-	-
Cu6				-	J6	J5	J3
Cu5'					-	J4	J2
Cu4'						-	J1
Dy'							-

A coupling model has been employed with the topological matrix for pair interactions as shown in Table S9 referring to the core of **1** (Fig. S10). In order to avoid an overparametrization, only two exchange interactions were considered in the fitting procedure, namely $J_{\text{Dy-Cu}} = J1 = J2 = J3$, and $J_{\text{Cu-Cu}} = J4 = J5 = J6$. The total number of basis set functions is $N = 16^2 \cdot 2^5 = 8192$; such a big interaction matrix can be factored, using the apparatus of the irreducible tensor operators, according to the molecular $J = 1/2$ through $35/2$ to smaller matrices of the dimension 20, 30, 32, 32, 32, 32, 32, 32, 32, 32, 32, 32, 32, 31, 26, 16, 6 and 1 (see also SI). In this model the molecular J is a "good quantum number" and the Zeeman term need be applied assuming uniform g-factors, g_{eff}. Otherwise, off-diagonal matrix element will appear and the blocking loses its advantage. The fit can be improved by considering more parameters such as different coupling constants and the temperature-independent magnetism. Involvement of different g-factors and Stevens operators will cause a return to the high-dimensionality problem that is not tractable nowadays.
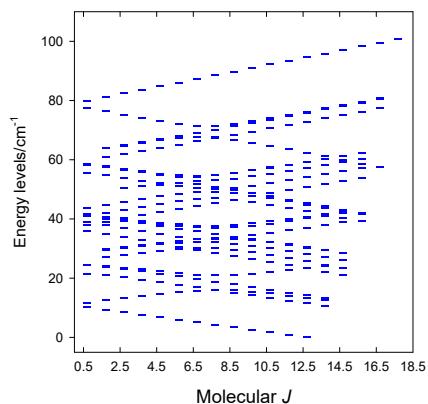
Fig. S8 Calculated spectrum of zero-field energy levels for **1** (482 entries).

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AC magnetic data
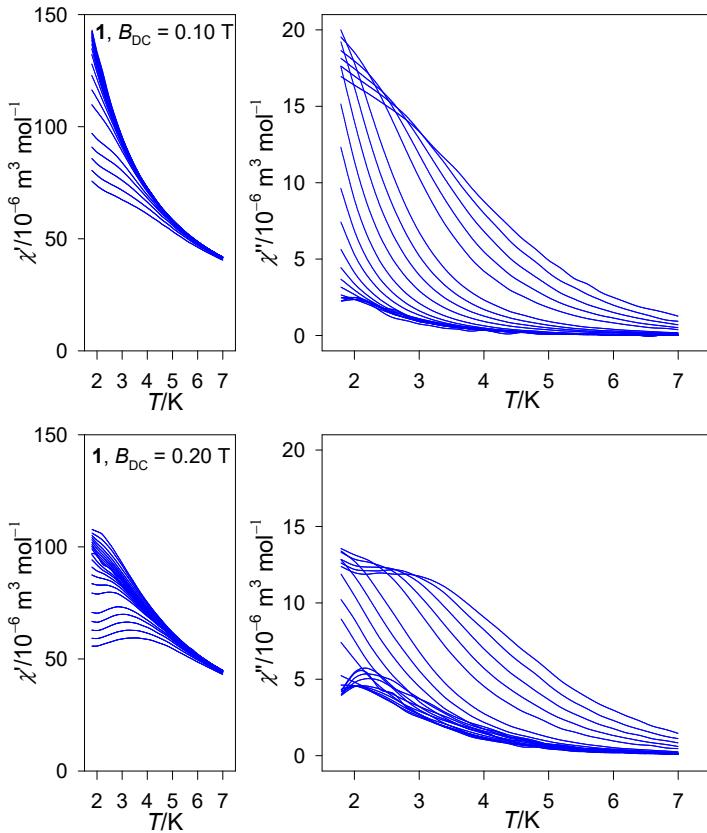
Fig. S9 Temperature dependence of the AC susceptibility for **1**.
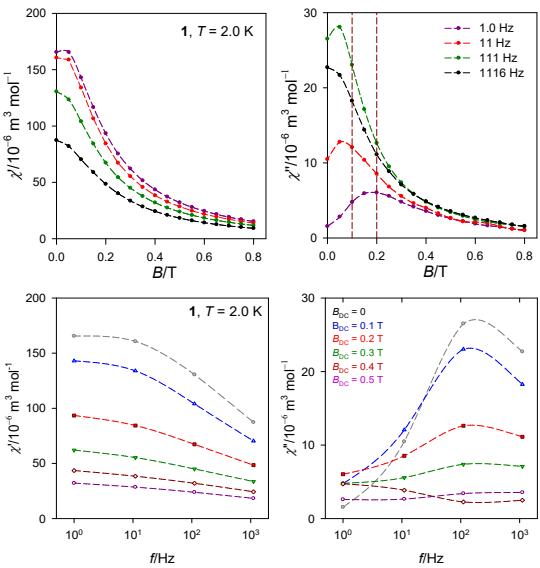
Fig. S10 Field and frequency dependence of the AC susceptibility at $T = 2.0$ K. Lines are guide for eyes. Verticals identify the B_{DC} used for the detailed frequency dependence.

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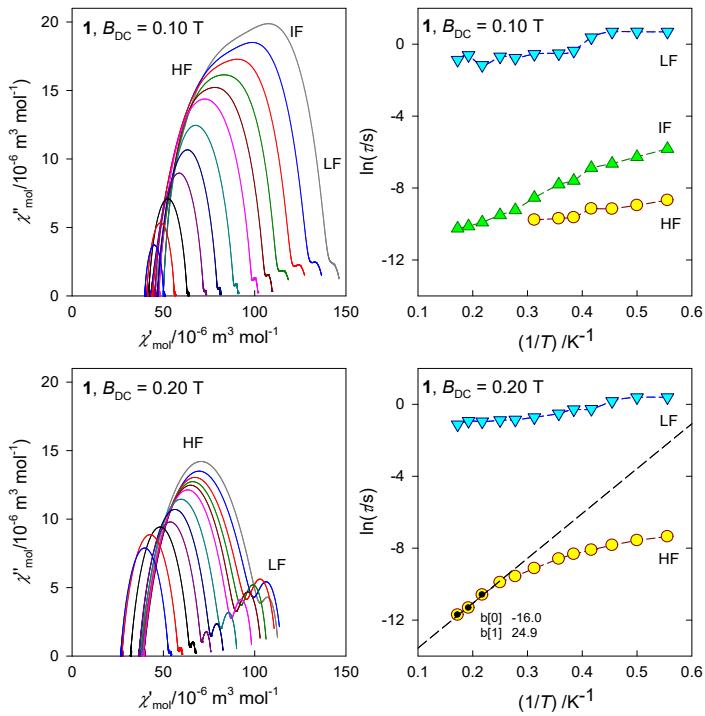
Fig. S11 Argand diagram (left) and Arrhenius-like plot (right) for **1**: $U_{eff}/k_B = 24.9$ K, $\tau_0 = 1.1 \times 10^{-7}$ s at $B_{DC} = 0.2$ T.

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Table S7. Temperature dependence of AC susceptibility parameters for **1** at B_{DC} = 0.1 T. [a]

| T/K	R(χ) /%	R(χ″) /%	χ$_S$	χ$_{LF}$	α$_{LF}$	τ$_{LF}$ / s	χ$_{IF}$	α$_{IF}$	τ$_{IF}$ /10^{-3} s	χ$_{HF}$	α$_{HF}$	τ$_{HF}$ /10^{-6} s	x$_{LF}$	x$_{IF}$	x$_{HF}$
1.8	0.64	0.97	45(15)	52(31)	.37(9)	2(4)	79(70)	.15	3(8)	147(9)	.46(2)	170	.07	.26	.67
2.0	0.17	0.71	43(3)	51(7)	.40(2)	2(1)	74(16)	.14(7)	2(1)	138(2)	.45(6)	127(47)	.09	.24	.67
2.2	0.43	0.65	44(9)	53(20)	.45	2(3)	74(48)	.15	1(3)	129(7)	.41(2)	104	.11	.25	.64
2.4	0.28	0.81	46(7)	55(13)	.49(3)	1(1)	73(40)	.14	1(3)	120(4)	.36(2)	105(96)	.11	.25	.64
2.6	0.21	0.74	50(8)	54(7)	.25(1)	.56(1)	90(20)	.26(2)	.50(1)	109(4)	.14	56(15)	.07	0.61	.33
2.8	1.0	0.60	47	50	.18	.59(4)	80	.27(2)	.41	101(1)	.21	61	.06	.54	.40
3.2	0.18	0.52	50(4)	52(4)	.21(1)	.57(1)	84(26)	.27(1)	.19(1)	90(2)	.0027	57(23)	.05	.78	.17
3.6	1.88	1.32	49	50	.20	.46	83	.26	.10	82(2)	.29	30	.04	.99	-.03
3.6b	0.26	1.26	47(9)	-	-	-	48(1)	.19(1)	.46(1)	81(2)	.27(1)	98(5)	-	.04	.96
4.0b	0.20	0.68	45(9)	-	-	-	46(1)	.28(1)	.49(1)	73(2)	.24(1)	74(4)	-	.04	.96
4.6b	0.13	1.48	42(8)	-	-	-	42(8)	.04	.31(6)	63(6)	.24(1)	49(3)	-	.02	.98
5.2b	0.38	2.04	40(2)	-	-	-	41(2)	.23	.54	56(3)	.22(4)	40(13)	-	.02	.98
5.8b	0.25	1.29	40(1)	-	-	-	40(2)	.25	.41	50(1)	.21(4)	35(12)	-	.02	.98

[a] Obtained by the three-set Debye model.

Table S8. Temperature dependence of AC susceptibility parameters for **1** at B_{DC} = 0.2 T. [a]

T/K	R(χ) /%	R(χ″) /%	χ$_S$	χ$_{IF}$	α$_{IF}$	τ$_{IF}$ / s	χ$_{HF}$	α$_{HF}$	τ$_{HF}$ /10^{-6} s	x$_{LF}$	x$_{HF}$
1.8	0.81	4.2	36(2)	44(5)	.16	1.5(8)	113(3)	.50(2)	642(54)	.11	.89
2.0	0.79	4.0	37(2)	51(6)	.25(1)	1.5(7)	114(3)	.48(2)	516(46)	.18	.82
2.2	0.41	3.2	37(1)	52(3)	.26(6)	1.2(2)	111(2)	.47(1)	397(23)	.20	.80
2.4	0.32	2.9	38(1)	51(2)	.22(4)	.77(7)	106(7)	.45(1)	304(16)	.19	.81
2.6	0.27	2.1	39(9)	52(2)	.28(3)	.75(7)	103(6)	.42(1)	241(11)	.21	.79
2.8	0.21	1.8	38(8)	49(1)	.23(2)	.59(3)	98(3)	.41(9)	185(8)	.18	.82
3.2	0.21	1.4	37(1)	46(1)	.23(2)	.48(2)	90(2)	.39(1)	109(6)	.16	.84
3.6	0.22	1.3	36(1)	43(1)	.26(3)	.42(3)	82(2)	.36(1)	69(6)	.15	.85
4.0	0.31	2.0	36(2)	42(2)	.25(5)	.41(5)	76(3)	.34(2)	50(8)	.13	.87
4.6	0.28	2.4	35(3)	38(3)	.24(6)	.39(6)	67(2)	.32(2)	30(7)	.09	.91
4.6b	0.31	2.9	32(5)	35(5)	.31(8)	.38(8)	67(3)	.33(3)	25(8)	.09	.91
5.2	0.29	2.0	27(9)	29(9)	.31(1)	.39(1)	60(2)	.34(4)	12(7)	.06	.94
5.8	0.36	4.1	26(20)	28(20)	.37(2)	.32(2)	54(3)	.31(8)	8	.04	.96

[a] Obtained by the two-set Debye model; χ in units of 10^{-6} m^3 mol^{-1}; R(χ) and R(χ″) – discrepancy factors of the fit.

Table S9. Broken symmetry magnetic coupling analysis for **1**.

	J1	J2	J3
Cu1-Cu2	535.27	267.64	528.64
Cu1-Cu3	482.29	241.14	475.61
Cu2-Cu3	−74.80	−37.40	−71.64
Dy-Cu1	1.59	0.87	1.66

J1: (a) A.P. Ginsberg J. Am. Chem. Soc. 102 (1980), 111, (b) L. Noodleman J. Chem. Phys. 74 (1981), 5737, (c) L. Noodleman E.R. Davidson Chem. Phys. 109 (1986), 131.

J2: A. Bencini D. Gatteschi J. Am. Chem. Soc. 108 (1980), 5763.

J3: (a) K. Yamaguchi Y. Takahara T. Fueno in: V.H. Smith (Ed.) Applied Quantum Chemistry. Reidel, Dordrecht (1986), pp 155, (b) T.Soda et al. Chem. Phys. Lett., 319, (2000), 223.

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Cartesian coordinates of fragments corresponding to individual metal centers used for TD-DFT calculations

Fragment of the Cu-4 center:

Br	12.77000	9.81500	16.16900
Cu	12.36700	8.38100	8.93300
O	13.26700	9.07100	7.34600
O	11.38100	8.02800	10.58200
O	9.61000	7.74800	12.45800
O	10.75500	7.63000	8.08400
N	13.92200	8.96900	9.88800
C	14.23500	11.23100	7.76900
C	14.50700	9.74400	7.66700
H	15.16500	9.58500	6.93200
C	15.05200	9.13500	8.96200
H	15.73500	9.73200	9.35900
H	15.47200	8.25900	8.77500
C	14.05500	9.19200	11.13300
H	14.90300	9.48000	11.44900
C	12.97900	9.03200	12.10100
C	13.27000	9.42800	13.42000
H	14.12200	9.78900	13.63400
C	12.32100	9.29100	14.39100
C	11.09000	8.75900	14.12800
H	10.44700	8.66600	14.82100
C	10.79700	8.36200	12.84300
C	11.74200	8.46700	11.80500
C	8.61100	7.67200	13.51300
H	8.43200	8.57300	13.85900
H	7.78300	7.29100	13.15400
H	8.94500	7.10500	14.23900
H	10.50385	8.19445	7.27239
H	9.98492	7.63467	8.75284
H	13.85814	11.58961	6.83397
H	15.14303	11.74411	8.00796
H	13.51175	11.40943	8.53710

Fragment of the Cu-5 center:

Cl	10.44500	10.94200	7.84600
Br	14.29300	15.77600	1.72700
Cu	12.28700	10.18200	6.06400
O	10.91400	11.74900	2.07300
O	11.60100	11.16800	4.51600
O	13.26700	9.07100	7.34600
O	11.14900	8.73600	5.41700
N	13.52600	11.56700	6.53600
C	12.23400	12.22100	3.96900
C	11.86700	12.57700	2.63900
C	12.45500	13.65100	1.98300
H	12.18400	13.89200	1.10500
C	13.43400	14.35700	2.63000
C	13.85200	14.03700	3.89600
H	14.53500	14.54600	4.31700
C	13.26300	12.94900	4.56500
C	13.80200	12.63100	5.86300
H	14.40700	13.25200	6.25200
C	14.23500	11.23100	7.76900
H	15.08100	11.74100	7.83700
H	13.67600	11.43300	8.56100
C	14.50700	9.74400	7.66700

Heptanuclear {Dy$_2$Cu$_5$} complex as a single-molecule magnet

Romana Mičová, Cyril Rajnák, Ján Titiš, Ján Moncoľ, Jana Nováčiková, Alina Bieńko and Roman Boča

H	15.16500	9.58500	6.93200
C	15.05200	9.13500	8.96200
C	10.11900	12.38000	1.02800
H	9.37000	11.79500	0.78900
H	9.77300	13.23700	1.35500
H	10.67900	12.53300	0.23900
H	14.35352	9.30045	9.75551
H	15.98611	9.59563	9.20726
H	15.19718	8.08338	8.82811
H	10.35937	8.61503	6.05123
H	11.68820	7.87112	5.37655

Fragment of the Cu-6 center:

Cu	9.68300	8.51000	6.71300
O	8.21700	8.28400	8.00800
O	8.61100	9.39000	5.34200
Cl	10.44500	10.94200	7.84600
O	11.14900	8.73600	5.41700
O	10.75500	7.63000	8.08400
Cl	8.92100	6.07800	5.58000
H	8.20075	9.08007	8.64551
H	8.36220	7.42564	8.53955
H	11.63909	9.61012	5.60707
H	10.76656	8.75923	4.47169
H	8.66470	10.40109	5.46537
H	7.64003	9.08856	5.42409
H	11.18249	8.33425	8.68541
H	11.48538	7.07378	7.63952

Fragment of the Dy center:

Dy	9.20800	7.34600	9.97800
Br	5.07200	1.24400	11.69900
O	8.45200	5.27200	11.35300
O	7.76500	5.85300	8.90900
O	8.21700	8.28400	8.00800
O	7.04400	7.83500	10.83200
H	6.68000	8.67000	11.03200
H	6.36900	7.22900	11.04300
O	10.62900	5.44400	9.82600
H	11.55000	5.40600	9.95000
H	10.38700	4.56800	9.62500
O	9.10500	9.70800	10.38700
H	9.09100	10.15700	9.61600
H	8.33200	9.92800	10.77200
N	5.84000	5.45300	6.89000
C	7.13200	4.79900	9.45700
C	7.49900	4.44300	10.78600
C	6.91100	3.36900	11.44300
H	7.18200	3.12900	12.32000
C	5.93200	2.66300	10.79600
C	5.51400	2.98300	9.53000
H	4.83100	2.47400	9.10800
C	6.10300	4.07100	8.86100
C	5.56300	4.38900	7.56300
H	4.95900	3.76800	7.17300
C	5.13100	5.78900	5.65600
C	9.24700	4.64000	12.39700
H	9.99600	5.22500	12.63600
H	9.59300	3.78300	12.07100

Heptanuclear {Dy$_2$Cu$_5$} complex as a single-molecule magnet
Romana Mičová, Cyril Rajnák, Ján Titiš, Ján Moncoľ, Jana Nováčiková, Alina Bieńko and Roman Boča

H	8.68700	4.48700	13.18700
Br	12.77000	9.81500	16.16900
O	11.38100	8.02800	10.58200
O	9.61000	7.74800	12.45800
O	10.75500	7.63000	8.08400
N	13.92200	8.96900	9.88800
C	15.05200	9.13500	8.96200
C	14.05500	9.19200	11.13300
H	14.90300	9.48000	11.44900
C	12.97900	9.03200	12.10100
C	13.27000	9.42800	13.42000
H	14.12200	9.78900	13.63400
C	12.32100	9.29100	14.39100
C	11.09000	8.75900	14.12800
H	10.44700	8.66600	14.82100
C	10.79700	8.36200	12.84300
C	11.74200	8.46700	11.80500
C	8.61100	7.67200	13.51300
H	8.43200	8.57300	13.85900
H	7.78300	7.29100	13.15400
H	8.94500	7.10500	14.23900
H	14.73545	8.90004	7.96727
H	15.84684	8.47818	9.24786
H	15.39603	10.14758	8.99700
H	5.51549	6.70664	5.26230
H	4.08708	5.89941	5.86320
H	5.27164	5.00680	4.93956
H	7.22848	8.46804	8.17931
H	8.31126	7.62650	7.23392
H	10.27924	7.38253	7.21635
H	11.56490	7.02344	8.21261