

Supporting Information for:

Unprecedented ferromagnetic dipolar interaction in a homobinuclear holmium(III) complex: A combined experimental and theoretical study

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Experimental Section

General Remarks:

All chemicals were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm⁻¹ on a Bio-Rad FTS-7 spectrometer.

Synthesis of [Ho₂(H₂cht)₂Cl₄(H₂O)(MeCN)]·MeCN (1**)**

A mixture of HoCl₃·6H₂O (0.113 g, 0.30 mmol), H₃cht (0.040 g, 0.30 mmol), and MeCN (8 mL) was sealed in a 25 mL Teflon-lined, stainless-steel vessel and heated at 160°C for 30 h, and then cooled to room temperature. The colorless crystals were obtained (yield ca. 43% based on H₃cht). C, H analysis calcd (%) for C₁₆H₃₀Cl₄Ho₂N₂O₇: C 23.04, H 3.62, N 3.36; found (%): C 23.39, H 3.88, N 3.59. Selected IR data (KBr, cm⁻¹): 3351 (s), 2943 (m), 1636 (s), 1413 (m), 1373 (w), 1324 (w), 1100 (s), 1072 (w), 1023 (m), 895 (m), 756 (w), 593 (m).

X-ray Crystallographic Study:

Diffraction intensities were collected on a Rigaku R-Axis SPIDER IP diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) for **1** at 150(2) K. The raw data frames were integrated with the Bruker SAINT package with a narrow frame algorithm.¹ An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program suite.² Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms attached to carbon were placed in idealised positions and refined using a riding model to the atom to which they were attached. The H-atoms attached to nitrogen and oxygen atoms were experimentally located from the Fourier difference maps and refined with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atoms. The ORTEP plots and packing pictures were produced with Diamond 3.1.³

CCDC reference numbers 859194.

Complex **1**: $M = 834.08$, monoclinic, $a = 15.505(3)$, $b = 9.277(2)$, $c = 8.885(2)$ Å, $\beta = 97.342(2)^\circ$, $V = 1267.5(4)$ Å³, $T = 123(2)$ K, space group $C2/m$, $Z = 2$, $\rho_c = 2.185$ g cm⁻³, $\mu = 6.656$ mm⁻¹, total data 3967, unique data 1268, $R_1 = 0.0196$ ($I > 2\sigma(I)$), $wR_2 = 0.0473$ (all data).

Magnetic measurements

Magnetic susceptibility measurements were performed with a Quantum Design MPMS-XL7 SQUID. Polycrystalline samples of **1** were embedded in vaseline to prevent torquing. All the ac susceptibility data were collected at zero dc field and 5 Oe ac amplitude. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

[1] Blessing, R. H.; *Acta Cryst.* **1995**, *A51*, 33.

[2] Sheldrick, G. M.; *Acta Cryst.* **2008**, *A64*, 112.

[3] Pennington, W.T.; DIAMOND, *J. Appl. Cryst.* **1999**, *32*, 1028.

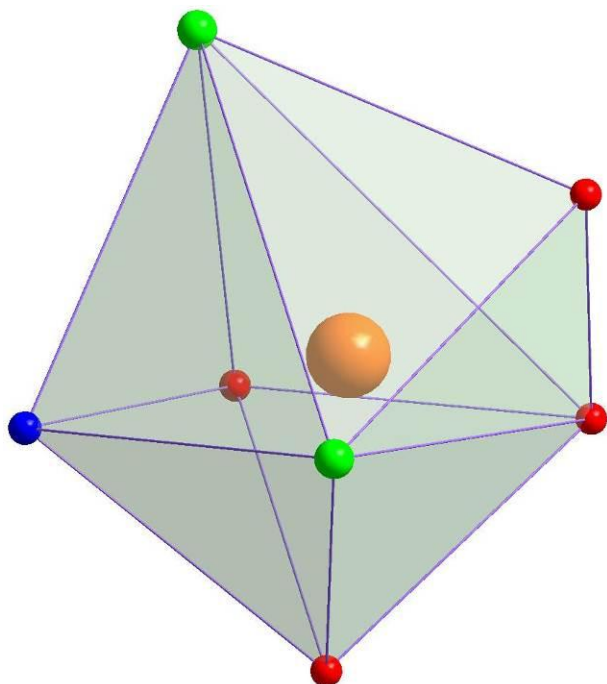


Figure S1. The coordination polyhedron of Ho1 in complex **1**.

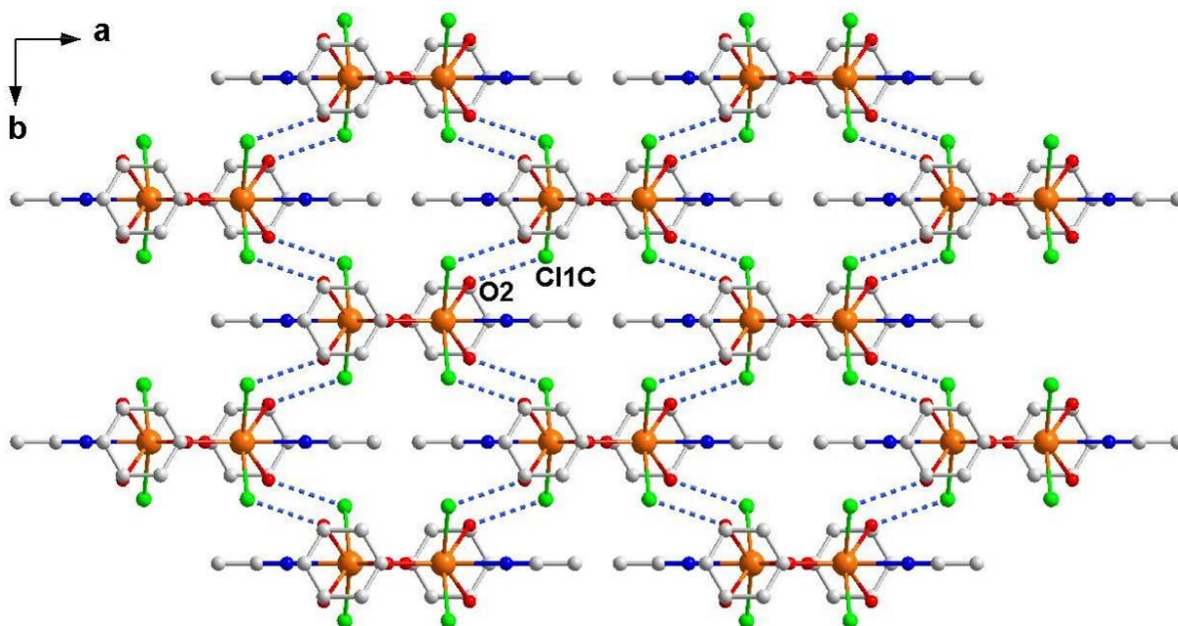


Figure S2. The packing arrangement of **1** viewed along *c* axis with inter-molecular H-bonds ($\text{O2} \cdots \text{Cl1C} = 3.091 \text{ \AA}$) shown as blue dashed lines. Symmetry code, C: $-x + 1/2, -y + 1/2, -z + 2$.

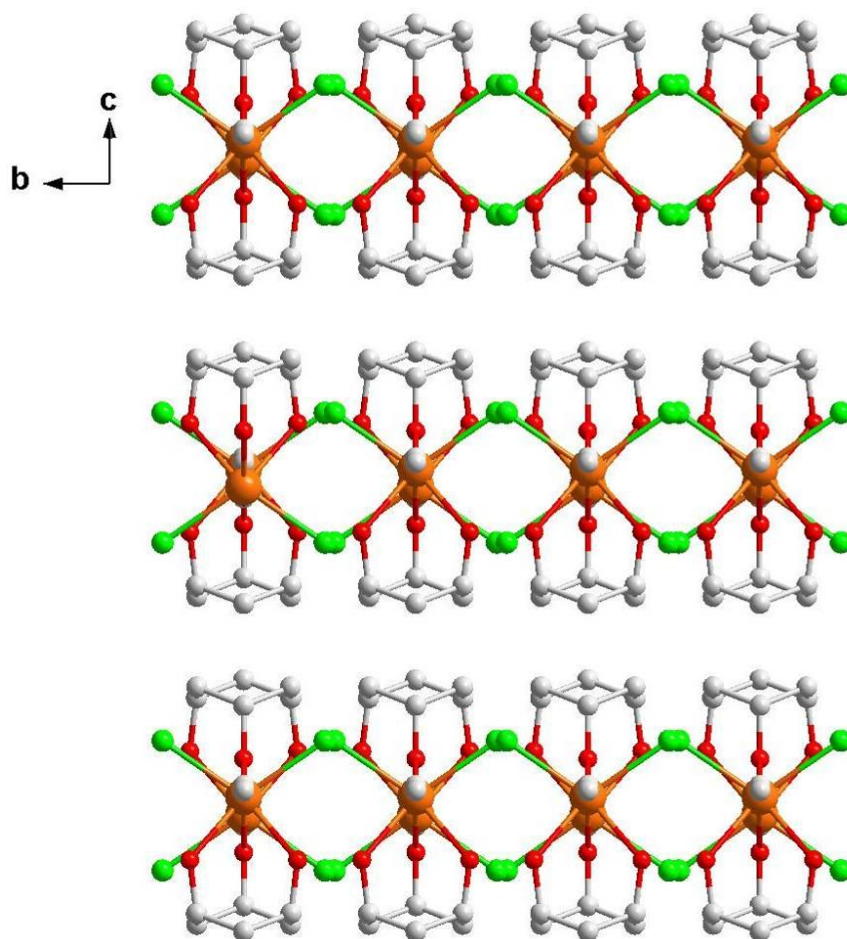


Figure S3. The packing arrangement of **1** viewed along *a* axis.

Computational Details

Energies and spin Hamiltonian parameters for low-energy states of Ho centres were obtained in a two step procedure: (i) RASSCF(10,7) calculation of spin-free energies and wavefunctions for models considering both Ho centres and replacing the remaining Ho position with a diamagnetic La^{III} ion, (ii) inclusion of spin-orbit coupling by a one-electron effective Hamiltonian considering the previously obtained spin-free states. This same procedure was followed for all calculated models (including structures from the CSD). No truncation of the geometry was performed in any model. A 9s8p6d4f3g2h ANO-RCC basis set was employed for Ho and La, 5s4p3d2f1g for Cl, 4s3p2d1f for O and N, 3s2p for C and 2s for H. For the RASSI matrix, we considered 35, 57 and 55 roots for the quintet, triplet and singlet states, respectively.

Table S1. Energy (cm⁻¹) of the lowest 17 states after the RASSI step for the studied Ho^{III} dinuclear complexes.

State number	1 (MeCN)	1 (H ₂ O)	IWAJOF	KAGXAT	IYIKUX
1	0	0	0	0	0
2	1.209	1.391	7.121	6.957	1.148
3	24.429	24.488	13.99	12.78	61.314
4	24.633	26.554	19.934	23.182	67.931
5	75.657	79.793	42.801	82.974	124.719
6	84.071	88.44	62.97	102.101	131.497
7	91.957	90.814	73.674	132.609	160.044
8	97.697	96.148	80.316	137.976	165.036
9	153.935	151.168	84.789	157.958	214.964
10	158.967	155.652	133.188	187.39	222.244
11	159.686	159.238	139.16	197.707	252.522
12	173.834	169.472	156.775	199.369	264.273
13	192.292	192.357	173.141	217.094	280.854
14	215.944	209.879	189.848	240.732	298.022
15	225.905	218.191	195.707	249.079	311.992
16	232.302	234.956	217.624	263.635	320.365
17	237.589	237.754	221.269	268.255	330.541

Table S2. Calculated *g* components at CASSCF-RASSI level corresponding to the Ho^{III} centers of the studied dinuclear Ho^{III} complexes.

	IWAJOF	IYIKUX	KAGXAT	1 (MeCN)	1 (H ₂ O)
<i>g</i> _x	0.000	0.000	0.000	0.000	0.000
<i>g</i> _y	0.000	0.000	0.000	0.000	0.000
<i>g</i> _z	12.905	18.594	15.619	17.371	17.681