SUPPORTING INFORMATION

Hard versus Soft: Zero-Field dinuclear Dy(III) oxygen bridged SMM and theoretical predictions of the sulfur and selenium analogues

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Experimental and Computational Methodology

All syntheses were performed under ambient conditions. All chemicals were commercially available and used as received.

Synthesis of $[HNEt_3][Gd_2(LH_4)_2(dbm)_2](NO_3)_3\cdot 2MeCN$ (1). To a colorless solution of dbmH (0.23 g, 1.0 mmol) and LH_5 (0.11 g, 0.5 mmol) in MeCN (20 mL) triethylamine (0.55 mL, 4.0 mmol) was added followed by stirring for 5 min. The reagent $Gd(NO_3)_3\cdot xH_2O$ (0.18 g, 0.5 mmol) was then added and the resulting pale yellow solution was stirred for an additional 1 hour. The solvent was then removed *in vacuo* and the resulting yellow solid was redissolved in MeOH/MeCN (20 mL, 1:1 v/v). The resulting solution was subsequently filtered and left to stand undisturbed for crystallization. Slow evaporation of the solvent gave diffraction quality crystals of **1** after 1 week which were collected by filtration, washed with hexanes (3 x 5 mL) and dried in air. Yield is 45%. Anal. Calc. for $C_{52}H_{74}N_6O_{23}Gd_2$ **(1)**: C, 42.61; H, 5.09; N, 5.73 %. Found: C, 42.55; H, 5.17; N, 5.62 %. Selected ATR data (Nujol mull, cm^{-1}): 1594 (m), 1552 (m), 1520 (m), 1374 (s), 1307 (w), 1221 (m), 1132 (m), 1105 (w), 1022 (m), 890 (w), 754 (m), 721 (m), 683 (w), 610 (w), 525 (w).

Synthesis of $[Dy_2(LH_4)_2(dbm)_2](NO_3)_2\cdot 2MeCN$ (2). This complex was prepared in the same manner as complex **1** but using $Dy(NO_3)_3\cdot 6H_2O$ (0.18 g, 0.5 mmol) in place of $Gd(NO_3)_3\cdot xH_2O$. After 1 week, diffraction quality crystals of **2** had appeared; these were collected by filtration and washed with hexanes (3 x 5 mL); the yield is 55%. Anal. Calc. for $C_{46}H_{58}N_4O_{20}Dy_2$ **(2)**: C, 42.11; H, 4.46; N, 4.27 %. Found: C, 42.20; H, 4.37; N, 4.21 %. Selected ATR data (Nujol mull, cm^{-1}): 1596 (m), 1550 (m), 1516 (m), 1377 (s), 1313 (w), 1221 (w), 1129 (w), 1102 (w), 1064 (w), 1025 (m), 892 (w), 750 (w), 720 (m), 685 (m), 608 (w), 523 (w).

X-ray Crystallography

Suitable crystals of compounds **1** and **2** were selected and mounted on microloops using ®Paratone oil under ambient conditions. Complete diffraction data were collected at 110.0 K for **1** and **2** on a Bruker D8 QUEST diffractometer equipped with a multilayer mirror monochromator and a MoKα microfocus sealed tube (λ = 0.71073 Å). The frames were integrated using the Apex II software program with a pre-existing mask supplied before collection.[1] A multiscan absorption correction was performed using SADABS within the APEX II software suite. The structures were solved with SHELXT[2] and refined with SHELXL-2014[3] within the OLEX program.[4] Dispersion corrections calculated in PLATON were applied to all structures for each element according to the wavelength of collection.[5] All hydrogen atoms were placed in calculated positions. All non-hydrogen atoms were finished with anisotropic refinement.

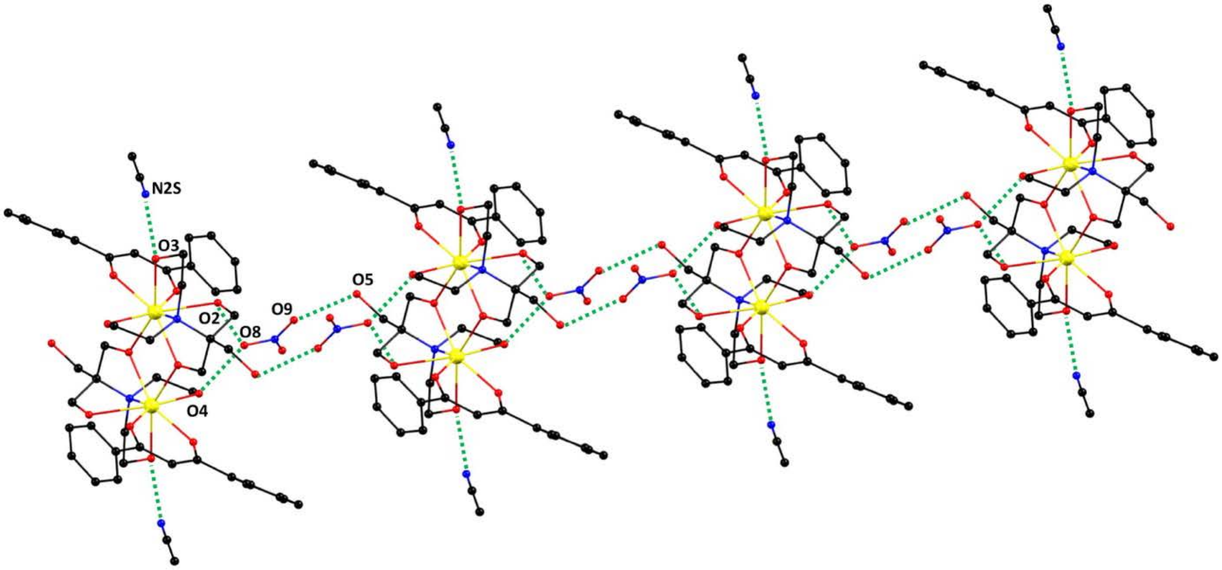

Figure S1. Intermolecular hydrogen bonding interactions in complex **2** (dashed green lines). The dimensions are: O(2)-H(2)···O(8) = 2.687(2) Å; O(4)-H(4)···O(8) = 2.685(2) Å; O(5)-H(5)···O(9) = 2.815(2); O(3)-H(3)···N(2S) = 2.843(2) Å. Color scheme: Dy, yellow; O, red; N, blue; C, black. H atoms were omitted for the sake of clarity.

Table S1. Crystal data and structural refinement parameters for compounds **1** and **2**.

Complex	**1. 4MeCN**	**2.MeCN**
Empirical formula	$C_{54}H_{77}Gd_2N_7O_{23}$	$C_{54}H_{70}Dy_2N_8O_{20}$
Formula weight	1506.72	1476.18
Temperature/K	110 K	110 K
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
a/Å	25.9973(9)	10.5842(3)
b/Å	12.6932 (4)	12.0661(4)
c/Å	19.6403(6)	12.7702(4)
α/°	90	63.514(10)
β/°	106.546(10)	85.6460(10)
γ/°	90	80.89(10)
Volume/Å^3	6212.7(3)	1441.27(8)
Z	4	1
λ / Å	0.71073	0.71073
Radiation type	Mo K_α	Mo K_α
ρ_{calc} / g cm^{-3}	1.611	1.701
μ / mm^{-1}	2.199	2.655
Measd / independent (Rint) reflns	72413/12791	24328/5474
Obsd reflns [$I > 2\sigma(I)$]	10737	5271
R_1[a]	0.0311	0.0152
wR_2[b]	0.0676	0.0385
GOF on F^2	1.068	1.120
$(\Delta\rho)_{max,min}$ / e Å^{-3}	1.017, -1.346	0.372, -0.743

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table S2. Shape measures of the 8-coordinate Gd1 and, Dy1 coordination polyhedra. The values in boldface indicate the closest polyhedron according to the Continuous Shape Measures.

Polyhedron[a]	Gd1	Dy1
OP-8	31.28	32.98
HPY-8	23.90	23.49
HBPY-8	15.55	14.67
CU-8	10.51	9.79
SAPR-8	2.69	3.65
TDD-8	**1.20**	**0.98**
JGBF-8	12.76	13.72
JETBPY-8	27.86	27.58
JBTPR-8	1.65	2.45
BTPR-8	1.36	1.91
JSD-8	2.90	3.10
TT-8	10.89	10.30
ETBPY-8	24.49	23.49

[a] Abbreviations: 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, Johnson biaugmented trigonal prism; BTPR-8, biaugmented trigonal prism; JSD-8, Johnson snub diphenoid; TT-8, triakis tetrahedron; ETBPY-8, elongated trigonal bipyramid.

Magnetic Measurements

Variable-temperature direct current (dc) magnetic susceptibility data were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet and operating in the 2-300 K range. The diamagnetic contribution of the polypropylene bag used to hold the sample was subtracted from the raw data. Pascal's constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibilities to give the molar paramagnetic susceptibilities (χ_M).

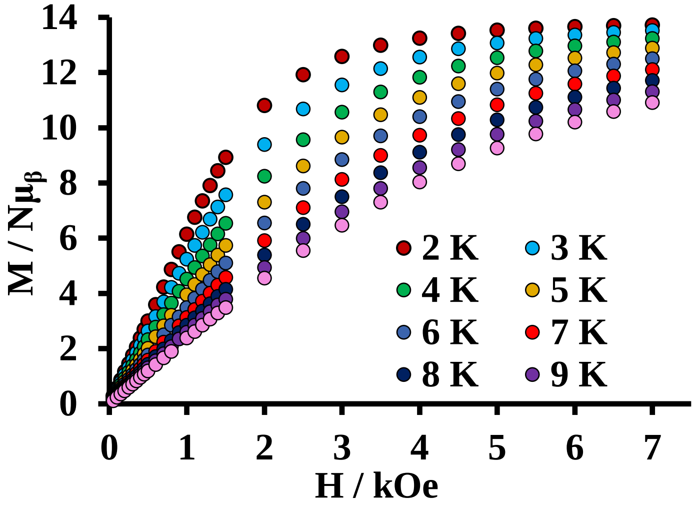

Figure S2. Plot of magnetization (M) vs field for complex **1** at different low temperatures.

Table S3. Cole-Cole fit values of **2** between 2-14 K under a zero *dc* field and an *ac* measuring field of 2.0 Oe.

T / K	χ_S / cm^3 mol^{-1}	χ_{t1} / cm^3 mol^{-1}	τ_1 / s	α_1	Residual
1.8	0.9150	60.9191	0.0603	0.1544	5.0604
2.67	0.9334	61.8507	0.0497	0.1444	7.9008
3.54	0.8701	55.9993	0.0411	0.1359	7.5304
4.41	0.7790	49.5707	0.0308	0.1234	6.5610
5.29	0.6813	43.8098	0.0194	0.1044	5.6106
6.16	0.5861	39.0583	0.0109	0.0858	4.3924
7.03	0.5245	35.2162	0.0061	0.0709	3.4027
7.9	0.5025	32.0787	0.0035	0.0611	2.5935
8.77	0.5226	29.4545	0.0021	0.0541	1.7894
9.64	0.5999	27.2201	0.0012	0.0474	1.2341
10.51	0.7306	25.2857	0.0007	0.0410	0.7734
11.39	0.8963	23.6072	0.0004	0.0351	0.4060
12.26	1.0869	22.1331	0.0002	0.0299	0.1884
13.13	1.2259	20.8423	0.0001	0.0275	0.1206
14	0.6012	19.6968	0.0001	0.0296	0.0975

Computational Details

DFT calculations were performed using the B3LYP functional[6] with *Gaussian 09* suite of programs[7] to compute the Gd^{III}–Gd^{III} magnetic interaction in complex **1** and to optimize the model complexes **2-S** and **2-Se** (see Figure SX below). The double-zeta quality basis set that employed Cundari–Stevens (CS) relativistic effective core potential on Gd atom[8] and Ahlrich's[9] triple-ζ-quality basis set were employed for the rest of the atoms. The following Hamiltonian is used to estimate the exchange interaction (*J*).

$$\hat{H} = -2J(S_{Gd1}S_{Gd2}) \qquad \text{Eq.1}$$

The Broken-Symmetry (BS) method[10] was employed as it has a proven record of yielding good numerical estimates of J constants for a variety of Gd based di-[11] and polynuclear complexes.[12] The PHI program[13] was used for the simulation of plots of magnetic susceptibilities vs temperature for **1**.

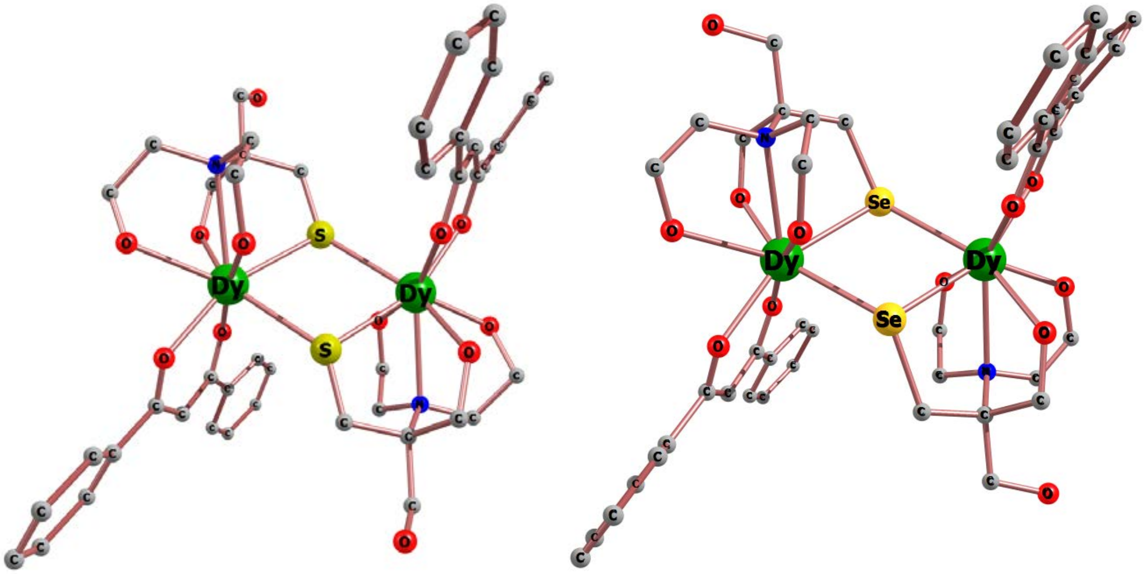

Figure S3. Optimized geometry of complexes (left) **2-S** and (right) **2-Se**. See at the bottom Table S10 and S11 for their coordinates used for *ab initio* calculations.

Using MOLCAS 8.0,[14] *ab initio* calculations were performed on the Dy(III) ions using its crystal structure. Relativistic effects are taken into account on the basis of the Douglas−Kroll Hamiltonian.[15] The spin-free eigen states are achieved by the Complete Active Space Self-Consistent Field (CASSCF) method.[16] The basis sets were taken from the ANORCC library for the calculations. We have employed the [ANO-RCC[17]... 8s7p5d3f2g1h.] basis set for Dy^{III} atoms, the [ANO-RCC...3s2p.] basis set for C atoms, the [ANO-RCC...2s.] basis set for H atoms, the [ANO-RCC...3s2p1d.] basis set for N atoms, the [ANO-RCC...7s6p4d2f.] basis set for the Lu atom, and the [ANO-RCC...3s2p1d.] basis set for O atoms. In the first step, we ran a guessorb calculation using seward module to create the starting guess orbitals. Here, we included nine electrons across seven 4f orbitals of the Dy^{III} ion. Then using these guess orbitals, we chose the active space based on the number of active electrons in the number of active orbitals and carried out the SA-CASSCF calculations. Here, the Configuration Interaction (CI) procedure was computed for the $\mathrm{Dy^{III}}$ ion and considered twenty-one sextet excited states, two hundred and twenty-four quartet excited states and four hundred and eighty doublet excited states in the calculations to compute the anisotropy. All the excited states corresponding to each multiplets of ions were computed in the CASSCF module. After computing these excited states, we mixed all the low-lying excited states (<50,000 $\mathrm{cm^{-1}}$) using the RASSI-SO[18] module to calculate the spin-orbit coupled states. Moreover, these computed SO states have been incorporated into the SINGLE_ANISO[19] program to compute the *g*-tensors. The *g*-tensors for the Kramers doublets of Dy(III) were computed based on the pseudospin S = ½ formalism.[19] Crystal-field (CF) parameters were extracted using the SINGLE_ANISO code, as implemented in MOLCAS 8.0. The CF parameters for complexes **2**, **2-S** and **2-Se** were analyzed for deeper insight into the mechanism of magnetic relaxation. The corresponding crystal field Hamiltonian is given in equation:

$$\hat{\mathrm{H}}_{\mathrm{CF}} = \sum \sum_{k=-q}^{q} B_k^q \tilde{\mathrm{O}}_k^q \text{ .... Eq.1}$$

where B_k^q is the crystal field parameter, while O_k^q is the Steven's operator.

The exchange/dipolar interactions between $\mathrm{Dy^{III}}$-radical and $\mathrm{Dy^{III}}$ -$\mathrm{Dy^{III}}$ have been computed by fitting with the experimental data using POLY_ANISO program.[20] The exchange Hamiltonian adapted for complexes **2**, **2-S** and **2-Se** are shown below.

$$\widehat{H_{ex}} = -\sum_{i=1}^{3} J_i . S_i . S_{i+1} \quad \text{……………………....................Eq.2}$$

(here $J_i = J_i^{dipolar} + J_i^{exch}$; i.e. J_i are the total magnetic interaction in combination of calculated $J_i^{dipolar}$ and fitted J_i^{exch} parameters; this describes the interaction between all the neighboring metal centers.)

Table S4. The *g*-tensor for the eight lowest Kramer’s doublets in **2**, **2-S** and **2-Se**.

KDs		Complex **2**		Complex **2-S**		Complex **2-Se**	
		Dy1	Dy2	Dy1	Dy2	Dy1	Dy2
1	g_x	0.0044	0.0044	0.0027	0.0026	0.0017	0.0013
	g_y	0.0072	0.0071	0.0037	0.0058	0.0020	0.0023
	g_z	19.6960	19.6830	19.7358	19.7057	19.7847	19.7741
2	g_x	0.1961	0.1957	0.1998	0.1990	0.1924	0.1130
	g_y	0.2678	0.2668	0.3660	0.3318	0.2995	0.1569
	g_z	16.8581	16.8802	14.9232	15.2070	16.2962	16.5895
3	g_x	2.6050	2.6023	0.0833	0.1625	0.4533	0.3647
	g_y	6.1219	6.1117	0.3683	0.5286	0.7055	0.5159
	g_z	9.9962	10.0043	12.7470	13.0806	14.7141	15.1614
4	g_x	2.3326	2.3449	0.9987	0.0775	1.3394	1.1116
	g_y	3.5681	3.5617	1.6968	0.8297	2.3085	1.9285
	g_z	11.3213	11.3090	11.0238	11.0872	11.3261	11.3828
5	g_x	3.6082	3.6160	2.9771	3.3825	1.4605	1.6211
	g_y	5.3867	5.3814	4.9937	3.6264	1.7849	3.2915
	g_z	12.5013	12.4937	8.4663	8.9093	8.1556	9.8438
6	g_x	0.7568	0.7579	0.9410	1.9857	3.5934	1.1483
	g_y	1.8244	1.8190	4.5425	4.7799	6.5281	3.2696
	g_z	15.5841	15.5683	11.3560	9.7974	10.2212	9.0072
7	g_x	0.2290	0.2269	2.0161	2.0626	0.7009	11.1289
	g_y	0.5569	0.5556	3.7770	4.4573	1.5365	7.8103
	g_z	16.5056	16.4991	14.2174	14.6387	15.7855	2.4679
8	g_x	0.0568	0.0567	0.4333	0.1906	0.0689	0.1650
	g_y	0.1369	0.1364	1.3951	0.4329	0.1449	0.4063
	g_z	18.5925	18.6254	18.4503	19.4390	19.5566	19.2062

Table S5. RASSI energies of the lowest spin-orbit states (cm^{-1}) of each Dy center in complex **2**, **2-S** and **2-Se**.

Complex **2**		Complex **2-S**		Complex **2-Se**	
Dy1	Dy2	Dy1	Dy2	Dy1	Dy2
0.000	0.000	0.000	0.000	0.000	0.000
158.004	157.999	117.957	121.646	201.170	217.884
314.975	314.983	192.740	201.870	315.277	353.295
380.111	380.107	311.494	309.834	428.895	438.125
437.327	437.356	413.385	397.017	535.177	522.021
513.934	513.904	504.755	480.979	596.254	583.025
589.663	589.686	556.108	541.334	672.144	635.852
697.858	697.887	635.252	649.044	830.372	762.794
3620.576	3620.569	3077.781	3080.256	3092.021	3099.720
3791.732	3791.743	3125.617	3128.331	3217.446	3228.659
3870.312	3870.298	3272.548	3261.605	3344.579	3347.108
3922.098	3922.093	3338.030	3324.516	3433.812	3439.198
3989.812	3989.826	3387.512	3373.364	3495.281	3496.572
4059.277	4059.269	3456.208	3450.620	3588.543	3566.848
4126.412	4126.407	3540.718	3548.232	3704.152	3641.691
6218.826	6218.816	5710.407	5700.155	5719.119	5732.114
6313.106	6313.096	5739.539	5747.917	5843.006	5835.486
6405.480	6405.448	5869.336	5853.955	5941.524	5942.128
6462.497	6462.500	5915.157	5907.171	6011.215	6016.131
6532.033	6532.038	5985.761	5985.963	6113.492	6101.638
6623.463	6623.446	6097.064	6092.647	6225.485	6178.652
8210.038	8210.022	7909.264	7904.158	7933.290	7945.659
8278.648	8278.615	7962.026	7958.362	8045.247	8033.553
8376.169	8376.140	8047.107	8038.728	8135.110	8137.971
8443.925	8443.931	8130.384	8129.478	8241.865	8237.004
8558.052	8558.036	8255.194	8247.757	8366.886	8328.414

9745.353	9745.325	9649.356	9643.231	9690.681	9695.750
9832.508	9832.468	9675.929	9676.736	9735.859	9735.253
9926.781	9926.755	9733.658	9724.028	9801.681	9791.499
10083.133	10083.118	9770.644	9769.781	9820.645	9816.925
10164.190	10164.180	9793.303	9786.269	9846.294	9841.054
10206.606	10206.580	9812.092	9804.330	9883.796	9871.654
10260.569	10260.542	9846.267	9832.303	9919.119	9913.066
10296.175	10296.142	9890.024	9880.615	9989.754	9971.590
10339.008	10339.001	9912.269	9904.745	10009.283	10006.565
10398.242	10398.251	10048.830	10044.291	10151.813	10116.992
10882.642	10882.625	11042.792	11040.597	11071.471	11081.403
11102.010	11101.963	11248.863	11233.838	11334.834	11339.903
11251.349	11251.331	11423.436	11421.124	11552.023	11503.418
11648.253	11648.223	11921.235	11913.072	11964.498	11960.416
11682.623	11682.600	11951.873	11943.078	12004.779	12000.498
11700.814	11700.811	11982.477	11976.619	12033.088	12021.196
11731.762	11731.749	12001.019	11991.191	12064.235	12049.125
11758.807	11758.792	12036.990	12026.975	12120.701	12108.133
13565.585	13565.539	13681.792	13677.450	13751.172	13743.638
13635.384	13635.366	13759.715	13749.198	13801.995	13792.109
13657.912	13657.886	13779.876	13771.636	13824.141	13815.566
13680.877	13680.856	13800.732	13789.438	13866.190	13852.678
15042.128	15042.086	15102.345	15099.047	15164.051	15154.362
15081.574	15081.541	15141.538	15128.287	15192.147	15185.933
15119.581	15119.555	15174.429	15165.193	15220.192	15206.000
15941.340	15941.304	16121.663	16111.879	16168.735	16160.897
15953.555	15953.521	16142.751	16133.983	16193.881	16180.768
16480.228	16480.191	16728.641	16719.650	16782.797	16770.567
38826.355	38826.265	38874.046	38857.522	38717.804	38739.925
38842.294	38842.212	38982.953	38968.989	38823.301	38828.128
38854.298	38854.216	39074.537	39060.890	38942.502	38944.533

38871.735	38871.653	39253.832	39233.823	39278.522	39265.418
38885.639	38885.563	40284.395	40267.281	40178.895	40188.866
38895.401	38895.316	40458.052	40438.186	40419.573	40430.903
38911.601	38911.516	40740.377	40726.418	40753.234	40697.281
38969.677	38969.603	41471.981	41455.847	41422.935	41402.799
39292.698	39292.602	41551.163	41534.493	41531.314	41506.310
39404.340	39404.256				
39543.910	39543.831				
39573.739	39573.648				
39620.130	39620.036				
39643.674	39643.589				
39667.031	39666.949				
39692.330	39692.242				
39722.418	39722.332				
39753.152	39753.063				
40238.628	40238.521				
40279.665	40279.560				
40439.985	40439.894				
40463.362	40463.268				
40530.010	40529.913				
40546.821	40546.734				
40554.888	40554.800				
40563.490	40563.397				
40577.277	40577.191				
40589.665	40589.577				
40606.150	40606.056				
40672.714	40672.627				
40708.558	40708.464				
40780.029	40779.948				
41093.979	41093.907				

Table S6. SINGLE_ANISO computed crystal field parameters for complexes **2**, **2-S** and **2-Se**. The major components in the Table are in bold. B_k^q is the crystal field parameter and O_k^q is the extended Stevens operator. The quantization axis is chosen to be the main magnetic axis of the ground pseudo-Doublet.

k	q	B_k^q	B_k^q	B_k^q	B_k^q	B_k^q	B_k^q
		Complex **2**		Complex **2-S**		Complex **2-Se**	
		Dy1	Dy2	Dy1	Dy2	Dy1	Dy2
2	-2	-0.06	-0.08	-1.03	-1.12	0.22	0.44
	-1	0.15	0.12	0.59	-0.38	-1.35	1.48
	0	**-3.07**	**-3.07**	**-2.68**	**-2.62**	**-3.65**	**-3.50**
	1	-1.00	-1.00	0.23	**1.22**	**3.42**	**-1.82**
	2	**1.85**	**1.85**	**3.03**	0.90	**3.03**	**2.21**
4	-4	-0.01	-0.01	-0.004	-0.005	-0.001	0.003
	-3	-0.05	-0.06	-0.02	-0.04	0.03	-0.02
	-2	-0.02	-0.02	-0.01	-0.03	0.007	0.005
	-1	-0.01	-0.01	-0.01	0.003	0.02	-0.02
	0	-0.004	-0.004	0.001	0.001	-0.002	-0.003
	1	0.02	0.02	-0.008	-0.007	-0.01	0.01
	2	-0.008	-0.008	0.03	0.008	0.02	0.01
	3	-0.01	-0.01	0.03	-0.001	0.02	-0.02
	4	-0.02	-0.02	-0.001	-0.007	0.005	0.003

Table S7. Lowest exchange coupled doublets (cm^{-1}) arising from the dipolar coupling, the corresponding tunnel splitting (Δ_{tun}, cm^{-1}), and the g_z value of each doublet (g_x and $g_y \neq 0$) for complex **2**.

No.	E(cm^{-1})	Δ_{tun}	g_z
1	0.000000000000 0.000000701675	7.0 x 10^{-7}	0.062056525
2	0.889656218020 0.889657205056	9.9 x 10^{-7}	39.378003799
3	158.199039935462 158.199313735541	2.7 x 10^{-4}	0.132250833
4	158.404542462927 158.406035563227	1.5 x 10^{-3}	0.039086195
5	158.513941175460 158.515402438791	1.5 x 10^{-3}	35.852623179

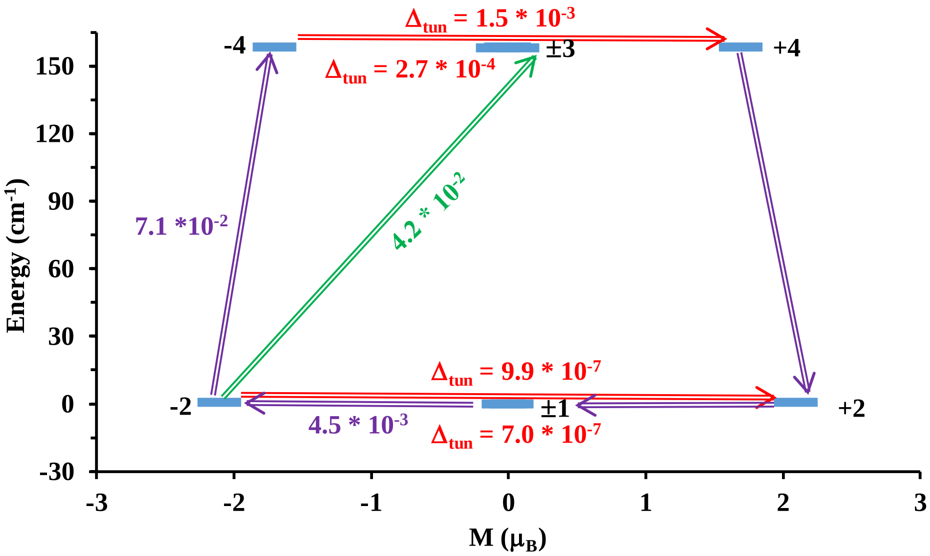

Figure S4. Low-lying exchange spectra in **2**. The exchange states are placed on the diagram according to their magnetic moments (bold black lines). The red arrows show the tunneling transitions (energy splitting) within each doublet state, while the green/blue arrows show the possible pathway through Orbach/Raman relaxation. The numbers at the paths are averaged transition moments in μ_B, connecting the corresponding states.

Table S8. Lowest exchange coupled doublets (cm^{-1}) arising from the dipolar coupling, the corresponding tunnel splitting (Δ_{tun}, cm^{-1}), and the g_z value of each doublet (g_x and $g_y \neq 0$) for complex **2-S**.

No.	E(cm^{-1})	Δ_{tun}	g_z
1	0.000000000000 0.000000147964	1.5 x 10^{-7}	1.877125805
2	0.586355715779 0.586356008714	2.9 x 10^{-7}	38.394173265
3	118.060245583197 118.060249440750	3.9 x 10^{-6}	5.056315171
4	118.438571942581 118.438580480875	8.5 x 10^{-6}	34.015569958
5	121.744425364885 121.744433993590	8.6 x 10^{-6}	7.062910997
6	122.135270228763 122.135294708621	2.4 x 10^{-5}	33.940841436
7	192.868503506130 192.868512540425	9.0 x 10^{-6}	7.273650403
8	193.198364562934 193.198372070747	7.5 x 10^{-6}	31.768419947
9	201.945011794504 201.945040220615	2.8 x 10^{-5}	6.790325100
10	202.381112561467 202.381148653773	3.6 x 10^{-5}	32.177365219
11	239.763005257130 239.763168870596	1.6 x 10^{-4}	2.496930237
12	240.029603151621 240.030307471582	7.0 x 10^{-4}	30.013312609

Table S9. Lowest exchange coupled doublets (cm^{-1}) arising from the dipolar coupling, the corresponding tunnel splitting (Δ_{tun}, cm^{-1}), and the g_z value of each doublet (g_x and $g_y \neq 0$) for complex **2-Se**.

No.	E(cm^{-1})	Δ_{tun}	g_z
1	0.000000000000 0.000000036778	3.7×10^{-8}	0.486630623
2	0.859708920108 0.859709913552	9.9×10^{-7}	39.255234874
3	201.250575535688 201.250576685652	1.1×10^{-6}	5.163490123
4	201.948695995204 201.948711390045	1.5×10^{-5}	35.753890049
5	217.952930919096 217.952933136430	2.2×10^{-6}	3.231185104
6	218.675714612459 218.675728782968	1.4×10^{-5}	36.152310615
7	315.413800972262 315.413814679196	1.4×10^{-5}	10.093745522
8	315.999278344170 315.999318211800	4.0×10^{-5}	33.244861981
9	353.432272485011 353.432287494396	1.5×10^{-5}	9.904259772
10	354.018274879105 354.018325283747	5.0×10^{-5}	33.594974249
11	419.185182780171 419.185203140113	2.0×10^{-5}	2.195293361
12	419.783195097828 419.783410277089	2.2×10^{-4}	32.810538339
13	533.331674243598 533.331807031464	1.3×10^{-4}	7.011865699

References:

1 Bruker-AXS, *Journal*, 2015.

2 G. M. Sheldrick, *Acta Crystallogr. Sect. A, Found. and Adv.*, 2015, **71**, 3-8.

3 G. M. Sheldrick, *Acta crystallogr. Sect. C, Struc. Chem.*, 2015, **C71**, 3-8.

4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.

5 A. Spek, *Acta Crystallographica Section D*, 2009, **65**, 148-155.

6 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.

7 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. P. Jr., F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, a. J. Cioslowski, D. J. Fox and I. Gaussian, Wallingford CT . *Journal*, 2009.

8 T. R. Cundari and W. J. Stevens, *J. Chem. Phys.*, 1993, **98**, 5555-5565.

9(a) A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571-2577;(b) A. Schaefer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829-5835.

10 L. Noodleman, *J. Am. Chem. Soc.*, 1981, **74**, 5737-5743.

11(a) T. Rajeshkumar and G. Rajaraman, *Chem. Commun.*, 2012, **48**, 7856-7858;(b) S. K. Singh, T. Rajeshkumar, V. Chandrasekhar and G. Rajaraman, *Polyhedron*, 2013, **66**, 81-86.

12(a) C. Das, S. Vaidya, T. Gupta, J. M. Frost, M. Righi, E. K. Brechin, M. Affronte, G. Rajaraman and M. Shanmugam, *Chem. Eur. J.*, 2015, **21**, 15639-15650;(b) K. R. Vignesh, S. K. Langley, B. Moubaraki, K. S. Murray and G. Rajaraman, *Chem. Eur. J.*, 2015, **21**, 16364-16369;(c) K. R. Vignesh, S. K. Langley, K. S. Murray and G. Rajaraman, *Chem. Eur. J.*, 2017, **23**, 1654–1666.

13 N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.*, 2013, **34**, 1164-1175.

14 F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. D. Vico, I. F. Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. L. Manni, H. Lischka, D. Ma, P. Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata and R. Lindh, *J. Comput. Chem.*, 2016, **37**, 506-541.

15 B. A. Hess, C. M. Marian, U. Wahlgren and O. Gropen, *Chem. Phys. Lett.*, 1996, **251**, 365-371.

16 B. O. Roos and P.-A. Malmqvist, *Phys. Chem. Chem. Phys.*, 2004, **6**, 2919-2927.

17 B. O. Roos, R. Lindh, P.-A. Malmqvist, V. Veryazov, P.-O. Widmark and A. C. Borin, *J. Phys. Chem. A*, 2008, **112**, 11431-11435.

18 P. A. Malmqvist, B. O. Roos and B. Schimmelpfennig, *Chem. Phys. Lett.*, 2002, **357**, 230-240.

19 L. F. Chibotaru and L. Ungur, *J. Chem. Phys.*, 2012, **137**, 064112-064122.

20 L. F. Chibotaru and L. Ungur, *POLY_ANISO program*, 2006, **University of Leuven**.

Table S10. Coordinates of the DFT optimised structure of complex **2-S**.

Dy	-1.80970	0.63690	-1.14070
S	0.24780	1.59250	0.56790
O	-2.80620	-0.47790	-2.87740
O	-2.86380	-0.52190	0.66930
H	-2.23330	-1.19720	0.98630
O	-1.29090	5.60720	1.84630
H	-1.52750	6.33810	2.43810
O	-0.67490	1.25280	-3.00610
C	2.70920	2.61620	-4.94220
H	3.40110	3.26930	-4.41740
C	-2.44120	-0.81680	-4.06890
C	-4.27890	2.82710	0.48230
H	-4.42950	3.88680	0.70570
H	-4.98970	2.28670	1.11060
C	1.60270	2.09420	-4.27600
H	1.42290	2.33970	-3.23410
C	-1.27920	-0.30610	-4.69000
H	-1.01100	-0.72180	-5.64920
C	-3.31010	-1.79000	-4.77630
C	-0.47590	2.95960	1.39810
H	0.20470	3.80980	1.34150
H	-0.50340	2.66420	2.44970
C	-1.87210	3.47480	0.94470
C	-5.02830	-3.50540	-4.64460
H	-5.69980	-4.11760	-4.04980
C	-3.29530	-1.93810	-6.17610
H	-2.65500	-1.31140	-6.78810
C	-4.19650	-2.58030	-4.02090
H	-4.21190	-2.46510	-2.94250
C	-4.13600	-2.85700	-6.79870
H	-4.12410	-2.95190	-7.88030
N	-2.89890	2.36470	0.85010
C	-0.47420	0.71870	-4.16890
C	0.90780	0.96730	-6.29720
H	0.20660	0.35540	-6.85360
C	-1.77800	4.13590	-0.45260
H	-2.62660	4.80690	-0.62180
H	-0.86820	4.73230	-0.51760
C	-2.26080	4.57930	1.96710
H	-3.26420	4.97460	1.75880
H	-2.27590	4.15050	2.98050
C	0.68720	1.25350	-4.93770
C	-5.00010	-3.64660	-6.03520
H	-5.65300	-4.36460	-6.52280
C	2.91960	2.31340	-6.29070
H	3.77690	2.72450	-6.81560
C	2.01320	1.49170	-6.96460
H	2.16120	1.26690	-8.01660

C	-3.57930	0.12610	1.74190
H	-3.55020	-0.50040	2.63830
H	-4.61760	0.19810	1.41010
C	-2.96860	1.49150	2.05560
H	-3.54980	1.95690	2.86650
H	-1.95940	1.32430	2.42780
O	-4.27390	1.25600	-1.31810
H	-4.66910	0.95610	-2.15480
O	-1.79740	3.13760	-1.49740
H	-1.06560	3.25350	-2.12830
C	-4.67490	2.59730	-0.97630
H	-5.76200	2.69530	-1.06810
H	-4.19620	3.30590	-1.65700
Dy	1.88560	-0.72250	1.17450
S	-0.17790	-1.68310	-0.52390
O	2.80620	0.47790	2.87740
O	2.86380	0.52190	-0.66930
H	2.23330	1.19720	-0.98630
O	1.29090	-5.60720	-1.84630
H	1.52750	-6.33810	-2.43810
O	0.67490	-1.25280	3.00610
C	-2.70920	-2.61620	4.94220
H	-3.40110	-3.26930	4.41740
C	2.44120	0.81680	4.06890
C	4.27890	-2.82710	-0.48230
H	4.42950	-3.88680	-0.70570
H	4.98970	-2.28670	-1.11060
C	-1.60270	-2.09420	4.27600
H	-1.42290	-2.33970	3.23410
C	1.27920	0.30610	4.69000
H	1.01100	0.72180	5.64920
C	3.31010	1.79000	4.77630
C	0.47590	-2.95960	-1.39810
H	-0.20470	-3.80980	-1.34150
H	0.50340	-2.66420	-2.44970
C	1.87210	-3.47480	-0.94470
C	5.02830	3.50540	4.64460
H	5.69980	4.11760	4.04980
C	3.29530	1.93810	6.17610
H	2.65500	1.31140	6.78810
C	4.19650	2.58030	4.02090
H	4.21190	2.46510	2.94250
C	4.13600	2.85700	6.79870
H	4.12410	2.95190	7.88030
N	2.89890	-2.36470	-0.85010
C	0.47420	-0.71870	4.16890
C	-0.90780	-0.96730	6.29720
H	-0.20660	-0.35540	6.85360
C	1.77800	-4.13590	0.45260
H	2.62660	-4.80690	0.62180
H	0.86820	-4.73230	0.51760

C	2.26080	-4.57930	-1.96710
H	3.26420	-4.97460	-1.75880
H	2.27590	-4.15050	-2.98050
C	-0.68720	-1.25350	4.93770
C	5.00010	3.64660	6.03520
H	5.65300	4.36460	6.52280
C	-2.91960	-2.31340	6.29070
H	-3.77690	-2.72450	6.81560
C	-2.01320	-1.49170	6.96460
H	-2.16120	-1.26690	8.01660
C	3.57930	-0.12610	-1.74190
H	3.55020	0.50040	-2.63830
H	4.61760	-0.19810	-1.41010
C	2.96860	-1.49150	-2.05560
H	3.54980	-1.95690	-2.86650
H	1.95940	-1.32430	-2.42780
O	4.27390	-1.25600	1.31810
H	4.66910	-0.95610	2.15480
O	1.79740	-3.13760	1.49740
H	1.06560	-3.25350	2.12830
C	4.67490	-2.59730	0.97630
H	5.76200	-2.69530	1.06810
H	4.19620	-3.30590	1.65700

Table S11. Coordinates of the DFT optimised structure of complex **2-Se**.

Dy	1.87680	1.41870	-0.31270
O	3.00450	-0.01500	-1.63240
O	3.90000	1.10500	0.71630
Se	0.70000	-0.46900	1.64000
O	-0.72600	-2.47170	-1.68590
O	0.16130	-5.88040	2.93420
O	-3.03420	-3.58300	0.00780
O	-1.95490	-2.38360	2.57280
N	-0.32070	-3.69340	0.79310
C	4.08380	-0.72730	-1.55730
C	4.30140	-1.69460	-2.66860
C	5.52460	-2.35560	-2.88260
C	5.67280	-3.25130	-3.93950
C	4.60450	-3.50360	-4.80340
C	3.38560	-2.84690	-4.60910
C	3.23730	-1.94960	-3.55470
C	4.99830	-0.61950	-0.49630
C	4.90530	0.30710	0.56380
C	5.98140	0.39840	1.58310
C	7.29120	-0.05710	1.34350
C	8.26990	0.05460	2.32810
C	7.95660	0.61600	3.56880
C	6.66070	1.07740	3.81750

C	5.68420	0.97730	2.83090
C	1.19520	-2.35000	2.34480
C	0.20360	-3.53710	2.21230
C	1.01110	-4.76450	2.72810
C	-1.03120	-3.35270	3.12090
C	0.74910	-3.73000	-0.25160
C	0.16900	-3.53130	-1.60970
C	-1.15920	-4.87180	0.62390
C	-2.42620	-4.80400	0.22520
H	6.37840	-2.15660	-2.24430
H	0.65560	-6.56510	3.41200
H	2.29890	-1.42670	-3.40080
H	7.56100	-0.46710	0.37590
H	-0.72120	-5.84350	0.82330
H	-0.71060	-3.03460	4.11680
H	-1.56810	-4.29580	3.21730
H	4.72450	-4.19890	-5.62890
H	4.67590	1.33150	3.01630
H	2.55800	-3.02910	-5.28940
H	1.50240	-4.47220	3.66710
H	1.80980	-4.99290	2.00610
H	0.74280	-3.74410	-2.50490
H	6.41520	1.51430	4.78120
H	6.62700	-3.74550	-4.09530
H	-3.04640	-5.68010	0.07130
H	2.14800	-2.57970	1.86450
H	1.45520	-2.91710	-0.03910
H	1.30770	-4.67650	-0.23850
H	5.84010	-1.29500	-0.48650
H	8.72070	0.69840	4.33620
H	9.27980	-0.28910	2.12540
H	1.40430	-2.21500	3.40770
Dy	-1.77450	-1.36350	0.37380
O	-3.00040	0.02040	1.62840
O	-3.89850	-1.10390	-0.71750
Se	-0.50860	0.38780	-1.64460
O	0.72750	2.46340	1.69080
O	-0.17940	5.87700	-2.92140
O	3.02870	3.58380	-0.00520
O	1.94990	2.38690	-2.57030
N	0.31350	3.68710	-0.78620
C	-4.07830	0.73470	1.55150
C	-4.29530	1.70330	2.66190
C	-5.51590	2.37070	2.87110
C	-5.66370	3.26700	3.92760
C	-4.59770	3.51340	4.79600
C	-3.38150	2.85040	4.60660
C	-3.23360	1.95270	3.55240
C	-4.99180	0.62750	0.48970
C	-4.90090	-0.30190	-0.56820
C	-5.97610	-0.39170	-1.58860

C	-7.28420	0.07070	-1.35250
C	-8.26200	-0.03980	-2.33810
C	-7.94960	-0.60680	-3.57650
C	-6.65540	-1.07510	-3.82180
C	-5.67990	-0.97610	-2.83400
C	-1.20010	2.34160	-2.33830
C	-0.21250	3.53180	-2.20500
C	-1.02480	4.75750	-2.71710
C	1.02170	3.35330	-3.11560
C	-0.75480	3.71850	0.26010
C	-0.17220	3.51920	1.61710
C	1.14850	4.86780	-0.61610
C	2.41630	4.80330	-0.21920
H	-6.36820	2.17650	2.22940
H	-0.67670	6.56090	-3.39720
H	-2.29740	1.42480	3.40240
H	-7.55360	0.48520	-0.38670
H	0.70720	5.83840	-0.81290
H	0.70080	3.03530	-4.11150
H	1.55490	4.29860	-3.21150
H	-4.71750	4.20920	5.62120
H	-4.67300	-1.33560	-3.01690
H	-2.55580	3.02790	5.29040
H	-1.51600	4.46550	-3.65630
H	-1.82370	4.98120	-1.99380
H	-0.74590	3.72820	2.51320
H	-6.41050	-1.51640	-4.78360
H	-6.61590	3.76620	4.07950
H	3.03400	5.68100	-0.06460
H	-2.15250	2.56640	-1.85480
H	-1.45890	2.90380	0.04750
H	-1.31650	4.66320	0.24950
H	-5.83190	1.30520	0.47790
H	-8.71290	-0.68830	-4.34480
H	-9.27050	0.30920	-2.13800
H	-1.41160	2.20910	-3.40110
H	-3.88710	-3.64030	-0.45220
H	-0.65400	-1.95130	-2.50940
H	-2.08300	-1.63280	3.17560
H	3.88100	3.64290	0.45570
H	0.65380	1.93720	2.51060
H	2.08010	1.63750	-3.17440
H	-1.47860	-4.79830	1.66350
H	-2.10730	-4.83840	-0.81650
H	-0.53080	-4.36660	-1.63580
H	1.46660	4.79730	-1.65630
H	2.09880	4.83460	0.82310
H	0.52410	4.35740	1.64400