Supporting Information

A Six-Coordinate Ytterbium Complex Exhibiting Easy-Plane Anisotropy and Field-Induced Single-Ion Magnet Behavior

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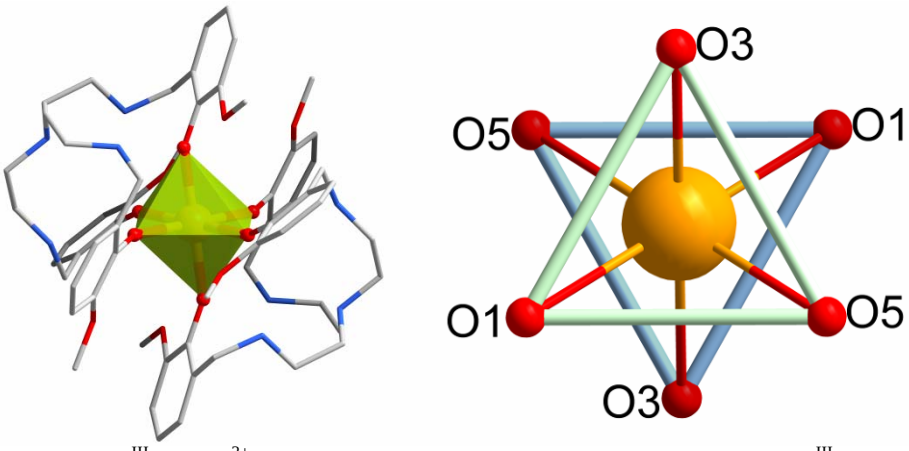

Figure S1 The structure of the $[Yb^{III}(\mathbf{H_3L})_2]^{3+}$ cation (*left*) and the coordination environment of Yb^{III} (*right*). The Yb^{III} is highlighted as a green polyhedron. Orange, gray, red, and blue spheres represent Yb, C, O, and N atoms, respectively Hydrogen atoms have been omitted for clarity.

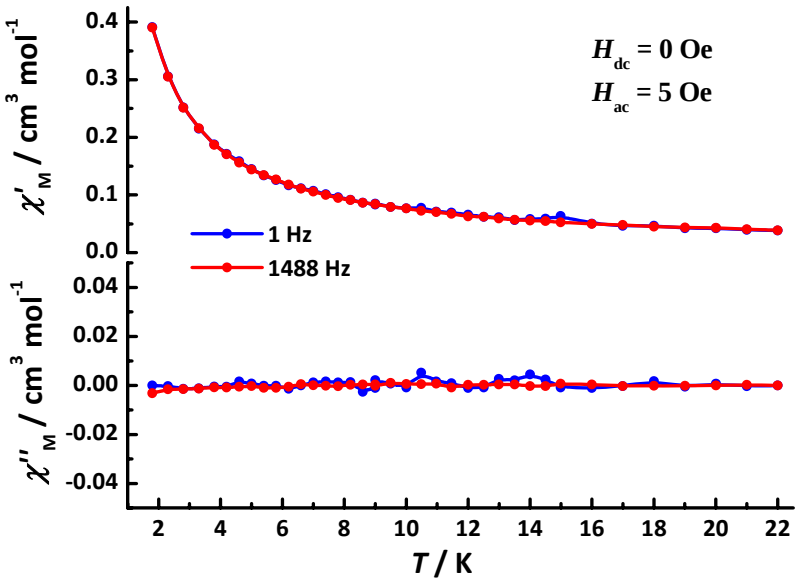

Figure S2 Plot of ac susceptibility *vs.* temperature oscillating at 1 Hz and 1488 Hz at H_{ac} = 5 Oe and H_{dc} = 0 Oe. The solid line is a guide for the eye.

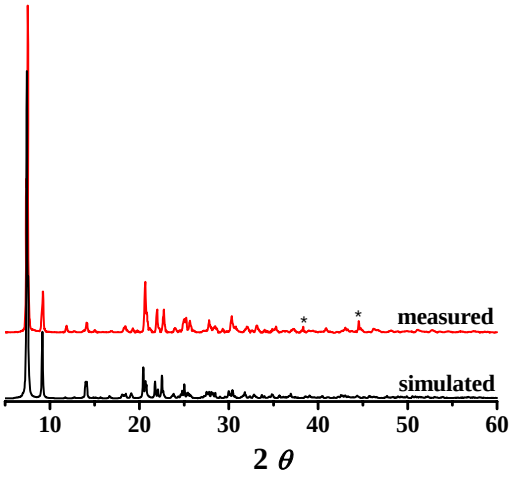

Figure S3 The powder X-ray diffraction pattern (red) and its simulation (black). The peaks marked with * were due to silicon carrier.

Ab initio calculations of electronic and magnetic properties of the Yb complex.

Computational details

All calculations were done with MOLCAS 7.6 and are of CASSCF/RASSI/SINGLE_ANISO type.
We have employed 7 structural approximations. The calculations were done on mononuclear Yb centers which were obtained from “cutting” a sufficiently large fragment from the initial complex, with subsequent saturation of all broken bonds by hydrogens.

The structural approximations of **A, B, C, D** are related to which H atoms attach to O, while **E, F, G** are related to which H attach to N.

A – a reduced fragment of the molecule (H atoms attach to O), **B** – a larger fragment (H atoms attach to O), **C** – a much larger fragment (H atoms attach to O), **D** – the entire molecule (H atoms attach to O), **D** – a reduced fragment of the molecule (H atoms attach to N), **E** – a larger fragment (H atoms attach to N), **F** – the entire molecule (H atoms attach to N)) and 2 basis set approximations (**1** – small and **2** – large), resulting in 14 computational approximations for the molecule (**A1**, **A2**, **B1**, **B2, C1, C2, D1, D2, E1, E2, F1, F2, G1** and **G2**)

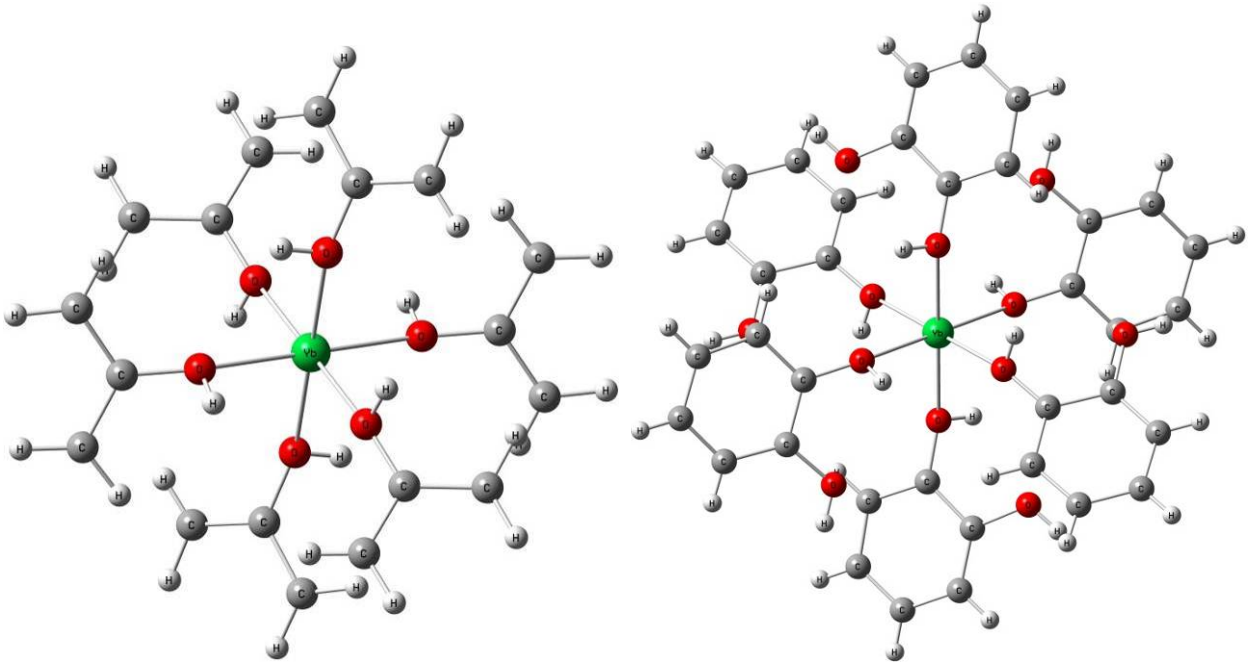

Figure S4 The structure of the calculated fragments **A** (left) and **B** (right) of the Yb center (H atoms attach to O).

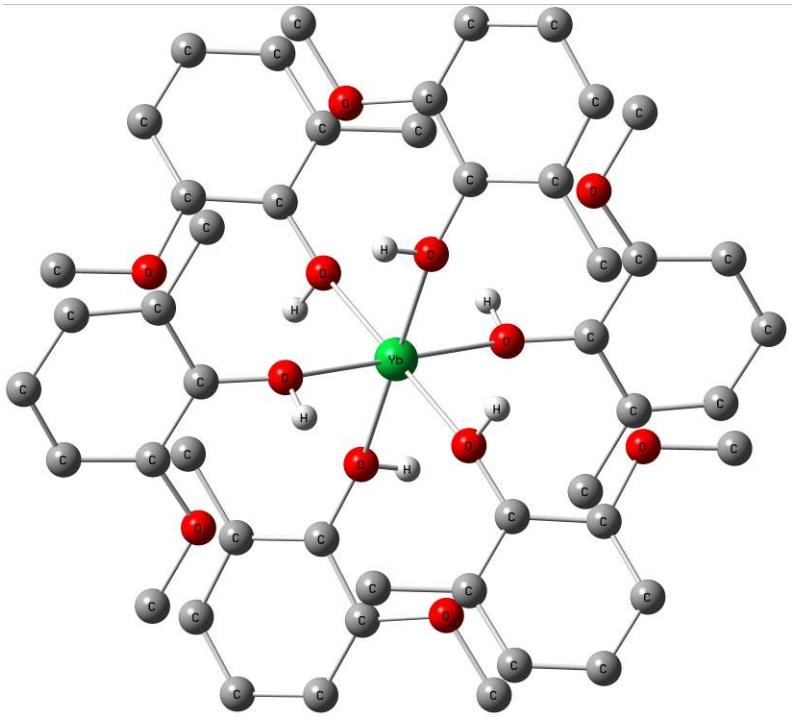

Figure S5 The structure of the calculated fragment **C** of the Yb center (H atoms attach to O). Hydrogen atoms are not shown.

Fragment **D** = entire molecule (H atoms attach to O).

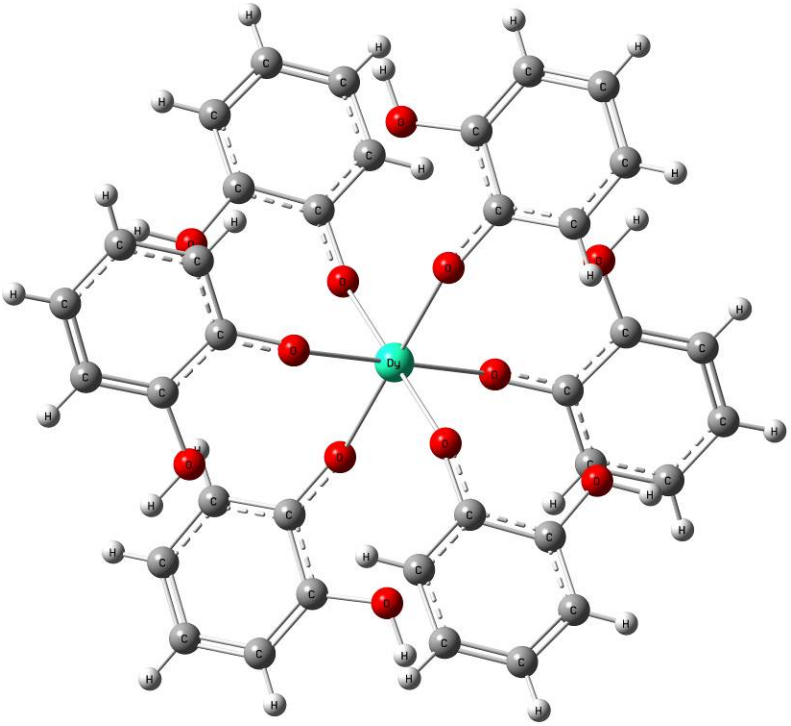

Figure S6 The structure of the calculated fragment **E** of the Yb center (H atoms attach to N).

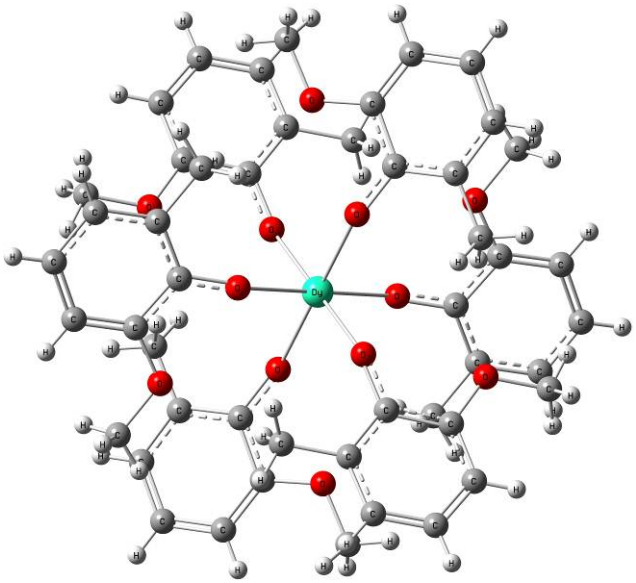

Figure S7 The structure of the calculated fragment **F** of the Yb center (H atoms attach to N).

Fragment **G** = entire molecule (H atoms attach to N).

Employed basis sets:
Basis1:
Yb.ANO-RCC...7s6p4d3f1g.
O.ANO-RCC...3s2p1d. (close)
O.ANO-DK3.Tsuchiya.12s8p.2s1p. (distant)
N.ANO-DK3.Tsuchiya.12s8p.2s1p.
C.ANO-DK3.Tsuchiya.12s8p.2s1p.
H.ANO-DK3.Tsuchiya.6s.1s.
Basis2:
Yb.ANO-RCC...8s7p5d4f2g1h.
O.ANO-RCC...4s3p2d. (close)
O.ANO-RCC...3s2p. (distant)
C.ANO-RCC... 3s2p.
N.ANO-RCC... 3s2p.
H.ANO-RCC...2s.

Results of the ab initio calculations:

Table S1. Energies of the spin-free states (cm^{-1}) on Yb center for all computational approximations.

2S+1	A	B	C		D	E		F		G	
	BS1	BS1	BS1	BS2	BS1	BS1	BS2	BS1	BS2	BS1	BS2
^2F	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	71.938	88.217	88.581	64.599	49.774	27.280	31.286	25.743	31.723	14.015	13.241
	126.718	133.450	135.820	113.570	87.714	29.706	37.726	29.101	36.604	37.595	37.700
	316.833	314.378	315.396	343.332	346.043	298.838	332.593	300.316	336.537	282.551	302.682
	562.182	571.926	573.690	548.362	477.403	323.664	345.299	324.514	345.458	370.434	387.988
	602.500	617.602	622.436	601.717	524.851	364.968	390.335	370.750	392.832	419.700	437.771
	641.348	651.449	656.668	677.234	572.017	469.727	531.228	478.208	537.565	524.968	570.621

Table S2. Energies of the lowest spin-orbit states (cm^{-1}) for all calculated Yb centers.

2S+1	A	B	C		D	E		F		G	
	BS1	BS1	BS1	BS2	BS1	BS1	BS2	BS1	BS2	BS1	BS2
$^2F_{7/2}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	163.78	156.99	157.45	178.90	187.93	174.82	189.11	174.91	190.19	169.52	179.82
	349.47	354.80	356.76	342.36	300.02	216.55	226.26	219.71	227.26	253.18	261.45
	542.67	547.21	550.95	560.47	485.03	394.74	433.59	401.58	438.24	445.38	475.22
$^2F_{5/2}$	10402.59	10398.77	10396.16	10420.62	10420.54	10419.55	10429.70	10417.61	10429.46	10418.55	10434.12
	10521.52	10522.93	10522.19	10519.11	10484.84	10444.97	10460.57	10443.91	10461.54	10449.63	10465.88
	10826.59	10831.36	10832.46	10848.19	10768.12	10686.47	10730.68	10689.90	10734.20	10727.19	10768.18

Table S3. *g*-tensors in all doublet states of the Yb center in all computational approximations.

KD	*g*	A	B	C		D	E		F		G	
		BS1	BS1	BS1	BS2	BS1	BS1	BS2	BS1	BS2	BS1	BS2
1	g_X	3.7633	3.5538	3.5994	3.5118	3.2098	1.9270	1.8864	1.9377	1.8995	2.0425	2.0454
	g_Y	2.7126	2.8980	2.8842	2.7288	2.6944	2.3928	2.4356	2.3964	2.4446	2.4108	2.3743
	g_Z	0.7223	0.4802	0.4491	1.2003	1.7634	3.5607	3.5568	3.5535	3.5341	3.4934	3.5272
2	g_X	1.7726	3.5110	3.5407	1.9261	1.9936	0.0319	0.4255	0.0830	0.4437	1.2694	1.1393
	g_Y	2.6684	2.8330	2.8290	2.5358	2.2654	1.4328	1.3627	1.4295	1.4493	1.6460	1.6016
	g_Z	3.8339	1.8262	1.7550	3.7150	3.6065	3.4839	3.3352	3.4446	3.2723	4.1142	4.1009
3	g_X	0.2607	0.3942	0.4241	0.3013	0.1556	0.3684	0.7414	0.3342	2.0493	0.1320	0.2051
	g_Y	0.8725	0.9741	1.0315	0.9149	0.7852	1.0150	1.3726	1.0213	1.4506	0.6523	0.5011
	g_Z	3.3019	3.2799	3.2686	3.2349	3.1483	2.4247	2.1382	2.3553	0.8498	2.9905	2.9946
4	g_X	4.8453	5.0057	5.0529	4.9185	1.8265	2.8463	2.8685	2.7690	2.7958	2.2896	2.3646
	g_Y	3.6174	3.4878	3.4355	3.4134	3.2849	3.0220	3.0964	3.0049	3.1266	3.0617	3.1373
	g_Z	1.3234	1.2781	1.2759	1.5251	4.8065	4.3108	4.2167	4.3912	4.2486	4.7648	4.6352
5	g_X	0.1805	0.0349	0.0595	0.1519	0.0924	0.1421	0.1275	0.2109	0.0618	1.1035	1.2191
	g_Y	0.9669	0.7940	0.8119	1.1259	1.3202	1.3939	1.3310	1.4224	1.2518	1.8315	1.7062
	g_Z	3.4371	3.4948	3.4965	3.2227	2.9302	2.9104	2.9428	2.9777	2.9587	2.8745	2.9300
6	g_X	0.2307	0.2440	0.2589	0.2417	0.2139	2.6703	0.6171	0.7442	0.5601	2.6613	2.6325
	g_Y	0.9361	0.7891	0.8359	1.0660	1.1448	1.7079	1.6233	1.6502	1.5581	2.0415	2.1576
	g_Z	2.5569	2.5409	2.5358	2.5114	2.4747	0.6646	2.6891	2.7553	2.6961	0.4625	0.5149
7	g_X	2.4481	2.5044	2.5252	2.4053	2.2865	0.9890	1.1034	0.9849	1.0794	0.5688	0.6409
	g_Y	1.8222	1.8238	1.8017	1.6622	1.5277	1.2459	1.2219	1.2093	1.2512	1.3968	1.3911
	g_Z	0.0170	0.0714	0.0710	0.1804	0.4436	2.0187	1.9210	2.0582	1.9149	2.2838	2.2118

Calculation of the magnetic properties with rescaled energy of the first excited Kramers doublet on Yb center up to 4.1 cm^{-1}:

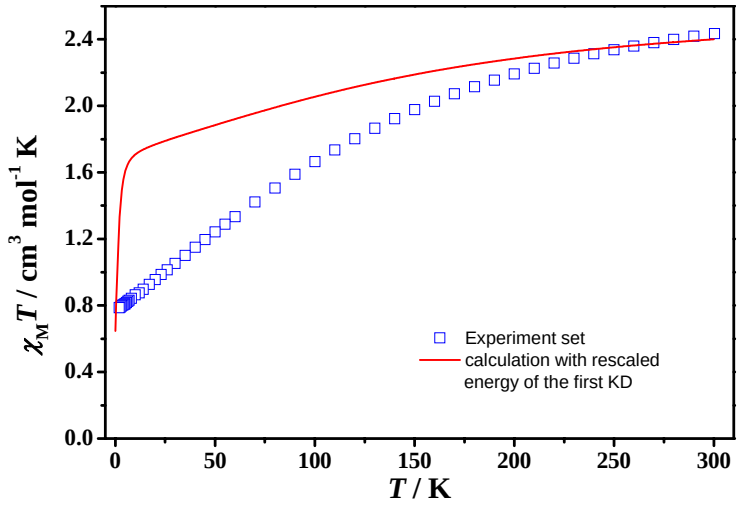

Figure S8 Comparison of the measured and calculated (with rescaled energy of the first excited KD on Yb center) magnetic susceptibility for computational approximation **D**.

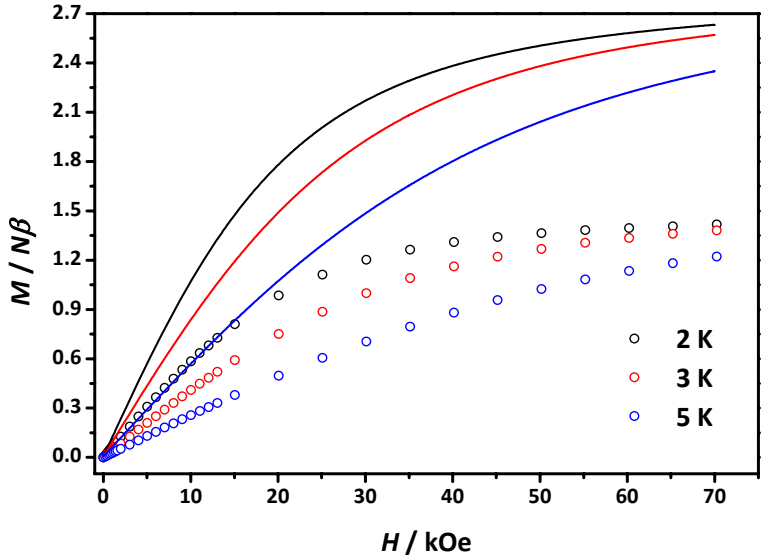

Figure S9 Comparison of the measured and calculated (with rescaled energy of the first excited KD on Yb center) molar magnetization at low temperature for computational approximation **D**.

The total disagreement between measured and calculated magnetism with rescaled energy of the first excited KD on Yb, proves the impossibility of having an excited state in this energy domain. Therefore the "barrier" extracted from the Arrhenius-like dependence of the relaxation time (the plot of log-reciprocal scale) does not correspond to an Orbach process. See text for detail.