Electronic Supplementary Information

The effect of the second coordination sphere on the magnetism of $[Ln(NO_3)_3(H_2O)_3]\cdot(18\text{-crown-}6)$ (Ln = Dy and Er)

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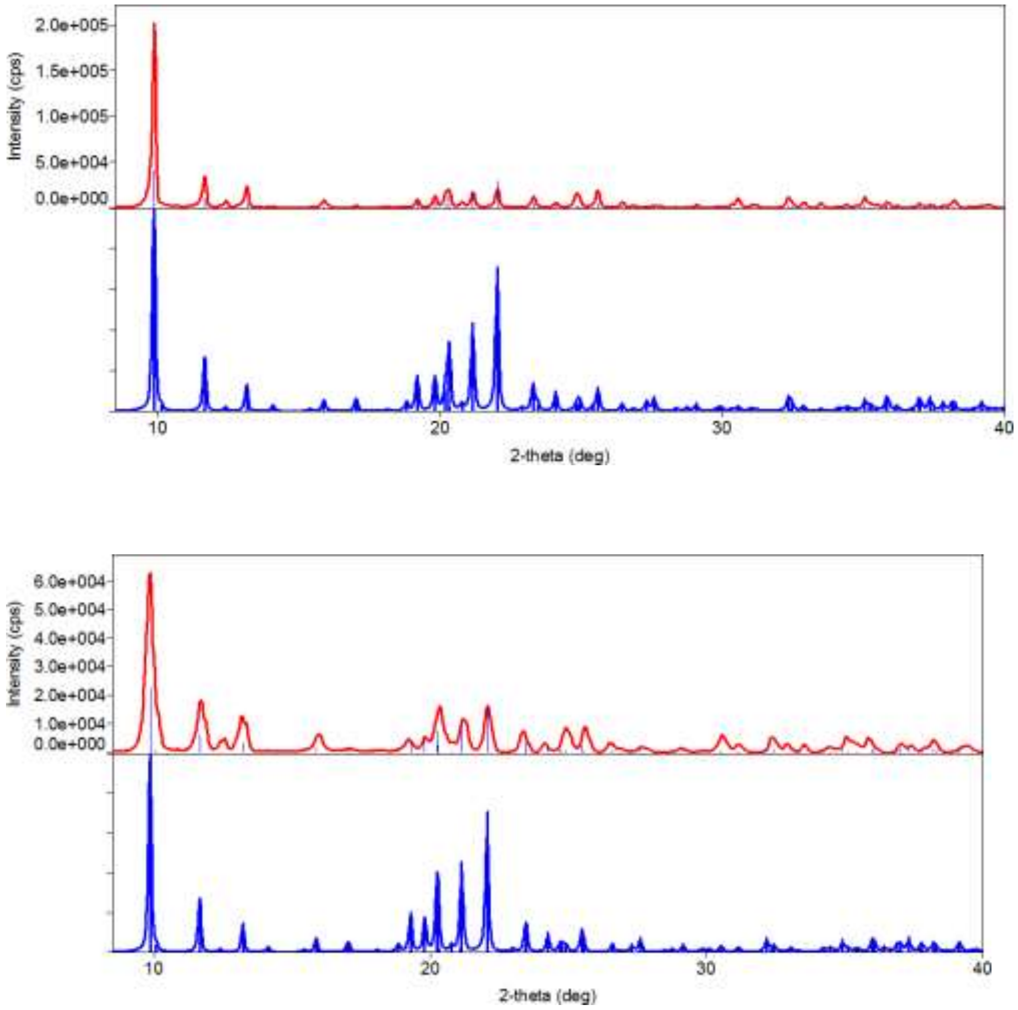


Figure S1. A comparison of the experimental (red) and calculated (blue) X-ray powder diffraction patterns of compounds 1 (top) and 2 (bottom).

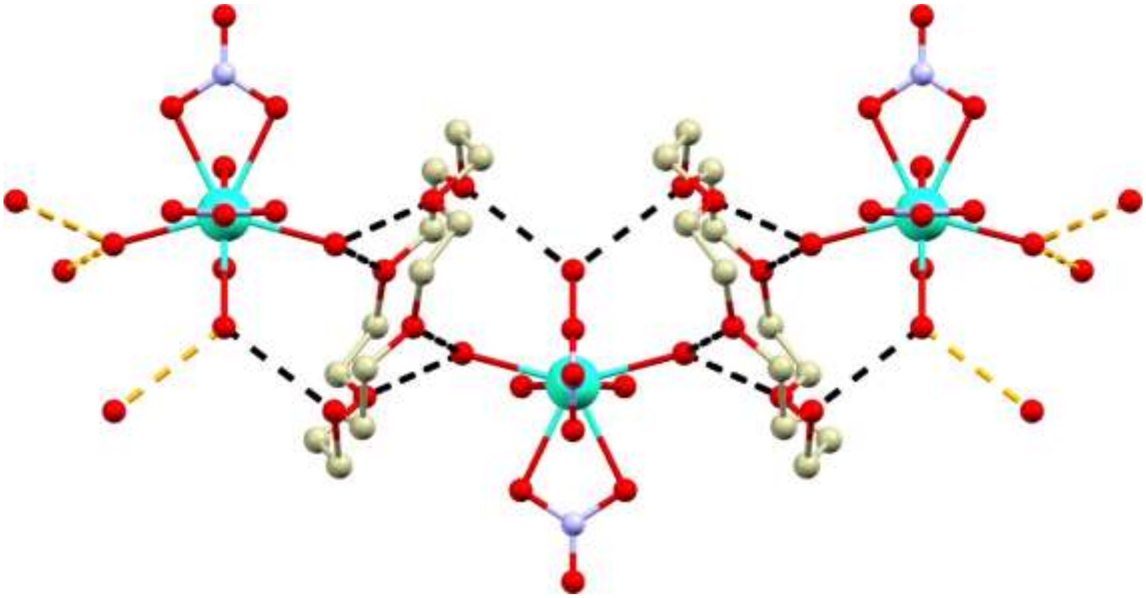


Figure S2. A perspective view on hydrogen bonding (black and gold dashed lines) in supramolecular 1D in motif of 1. (Hydrogen atoms were omitted for clarity).

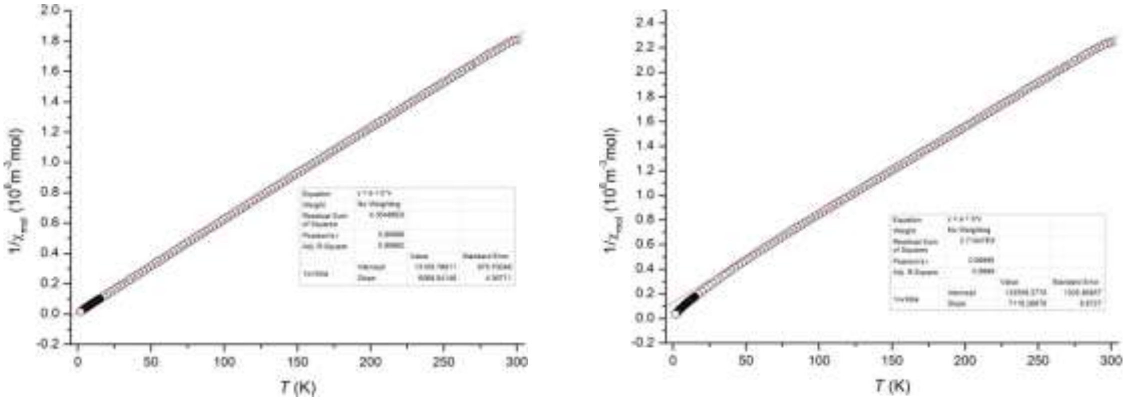
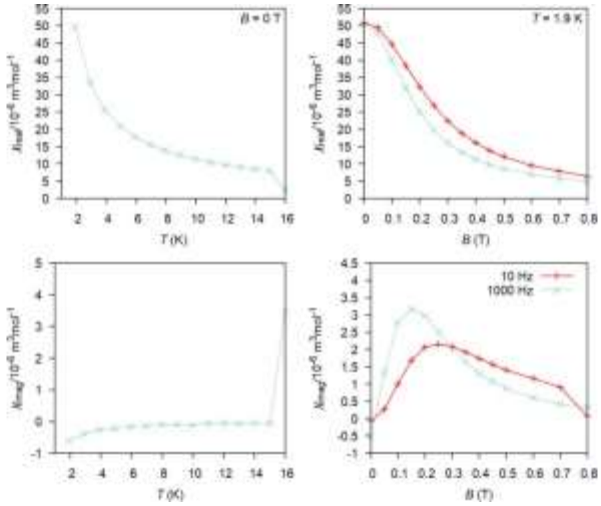


Figure S3 The analysis of the molar susceptibilities for compounds 1 (left) and 2 (right) with Curie-Weiss law. Empty circles – experimental data, full lines – calculated data.

1



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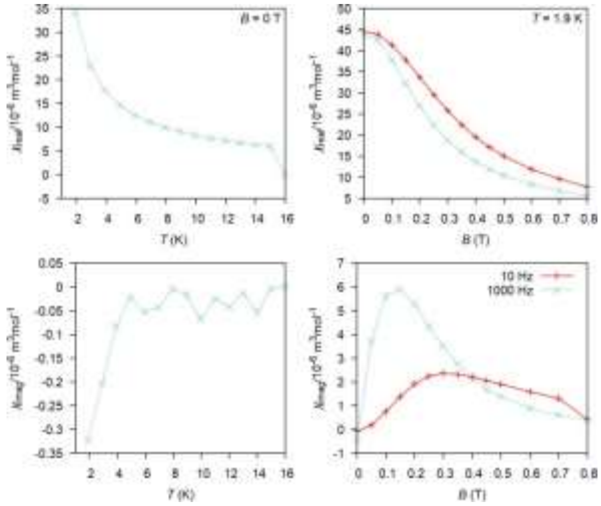

Figure S4 The in-phase χ_{real} and out-of-phase χ_{imag} molar susceptibilities for 1 and 2 at zero static magnetic field (left) and in non-zero static field (right).

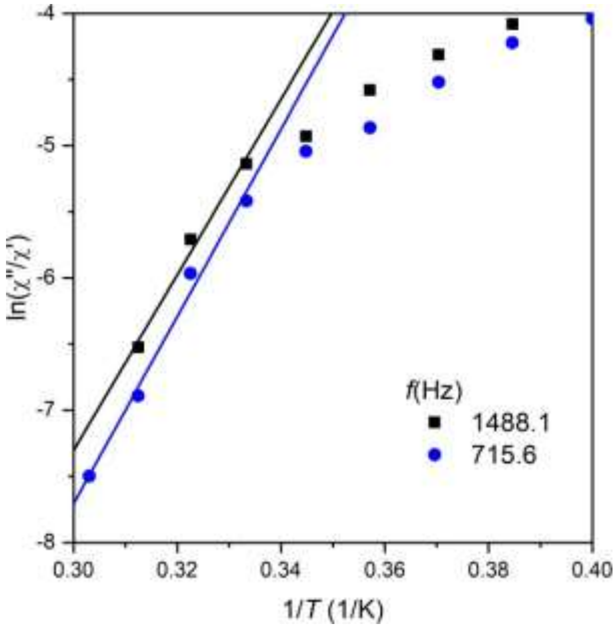

Figure S5. Analysis of ac molar susceptibilities for 1 measured at the applied external field B_{DC} = 0.1 T according to eq. 4. Full points – experimental data, full lines – calculated data. Black line for f = 1488.1 Hz: τ_0 = 1.58×10^{-16} s, U_{eff} = 66 K; blue line for f = 715.6 Hz: τ_0 = 5.89×10^{-17} s, U_{eff} = 71 K.

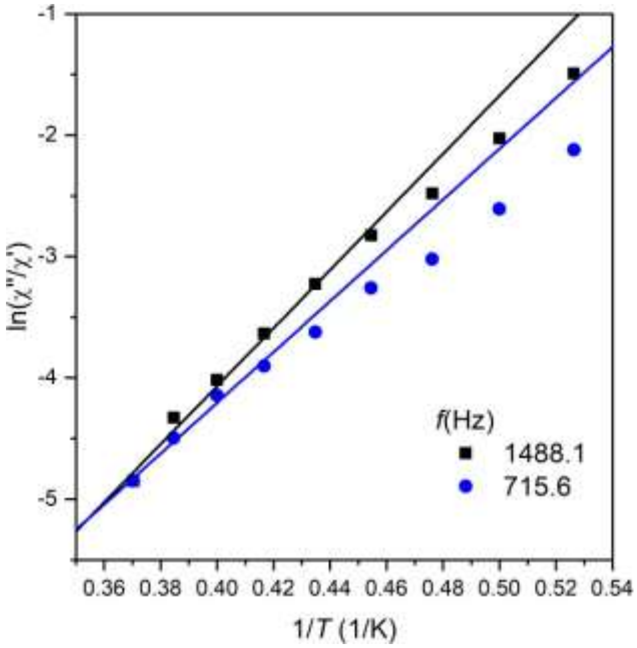

Figure S6. Analysis of ac molar susceptibilities for 2 measured at the applied external field BDC = 0.1 T according to eq. 4. Full points – experimental data, full lines – calculated data. Black line for f = 1488.1 Hz: τ_0 = 1.27×10^{-10} s, U_{eff} = 24 K; blue line for f = 715.6 Hz: τ_0 = 7.66×10^{-10} s, U_{eff} = 21 K.

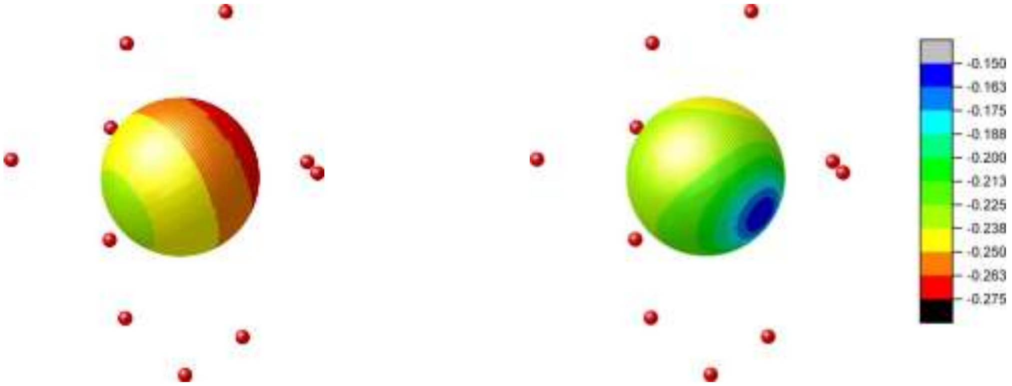

Figure S7 The electrostatic potentials of the ligands projected in a sphere of 1 Å radius located at the erbium position in molecular systems $[Er(NO_3)_3(H_2O)_3]$ (left) and $[Er(NO_3)_3(H_2O)_3]\cdot(18C6)_2$ (right) obtained by removing the erbium atom. The color scale of the electrostatic potential is shown on the right. The donor oxygen atoms from nitrato and aqua ligands are shown as red balls.

Table S1. Results of continuous shape measures calculations using program Shape 2.1 for complexes 1 and 2.[a]

	Dy(III), (**1**)	Er(III), (**2**)
CN = 9[b]		
EP-9	35.681	35.613
OPY-9	21.810	22.032
HBPY-9	19.562	19.582
JTC-9	15.009	15.066
JCCU-9	11.544	11.540
CCU-9	9.833	9.868
JCSAPR-9	3.380	3.130
CSAPR-9	2.117	1.889
JTCTPR-9	4.953	4.723
TCTPR-9	3.419	3.178
JTDIC-9	12.789	12.719
HH-9	9.837	9.920
MFF-9	**1.822**	**1.625**

[a] the listed values correspond to the deviation between the ideal and real coordination polyhedra, the lowest values are in red color.

[b] EP-9 = enneagon, OPY-9 = octagonal pyramid, HBPY-9 = heptagonal bipyramid, JTC-9 = Johnson triangular cupola J3, JCCU-9 = capped cube J8, CCU-9 = spherical-relaxed capped cube, JCSAPR-9 = capped square antiprism, CSAPR-9 = spherical capped square antiprism, JTCTPR-9 = tricapped trigonal prism J51, TCTPR-9 = spherical tricapped trigonal prism, JTDIC-9 = tridiminished icosahedron, HH-9 = hula-hoop, MFF-9 = muffin.

Table S2 Energy levels (cm^{-1} or K) of the lowest ligand field multiplets in zero magnetic field derived from CASSCF/DKH2/SINGLE_ANISO calculations for [Dy(NO$_3$)$_3$(H$_2$O)$_3$] of compound 1 with respective g-factors derived for each Kramers doublet with effective spin 1/2.

Energy (cm^{-1})	Energy (K)	g_X	g_Y	g_Z
0	0	0.0252	0.0486	19.4760
99	143	0.8804	1.4250	18.0576
153	220	2.4375	5.7563	9.2346
182	262	8.5546	5.5258	1.9440
213	307	3.7163	4.2227	10.6437
235	339	0.0289	1.5164	14.8111
266	383	0.5292	0.8806	15.4796
299	430	0.2955	1.3271	17.8739

Table S3 Energy levels (cm^{-1} or K) of the lowest ligand field multiplets in zero magnetic field derived from CASSCF/DKH2/SINGLE_ANISO calculations for [Er(NO$_3$)$_3$(H$_2$O)$_3$] of compound 2 with respective g-factors derived for each Kramers doublet with effective spin 1/2.

Energy (cm^{-1})	Energy (K)	g_X	g_Y	g_Z
0	0	0.7041	3.7186	12.4823
30	42	2.8136	5.5864	9.3725
106	152	6.7373	4.9587	3.0869
142	204	0.1487	0.5238	15.6873
179	258	0.7251	1.2656	11.7257
221	317	0.5446	1.0821	4.7261
279	401	4.1726	4.7322	6.1666
324	466	3.1832	3.5588	11.6421

Table S4 Energy levels (cm^{-1} or K) of the lowest ligand field multiplets in zero magnetic field derived from CASSCF/DKH2/SINGLE_ANISO calculations for $[Dy(NO_3)_3(H_2O)_3]\cdot(18C6)_2$ of compound 1 with respective g-factors derived for each Kramers doublet with effective spin 1/2.

Energy (cm^{-1})	Energy (K)	g_X	g_Y	g_Z
0	0	0.1050	0.5283	18.7563
40	57	0.2739	1.0270	16.2309
56	80	3.0165	4.4533	12.5439
89	128	0.2341	3.2065	14.0541
104	149	0.0962	5.2411	11.9038
153	221	2.2987	3.0202	11.1354
222	319	0.2804	0.8833	14.2856
274	394	0.4103	0.6105	17.3750

Table S5 Energy levels (cm^{-1} or K) of lowest ligand field multiplets in zero magnetic field derived from CASSCF/DKH2/SINGLE_ANISO calculations for $[Er(NO_3)_3(H_2O)_3]\cdot(18C6)_2$ of compound 2 with respective g-factors derived for each Kramers doublet with effective spin 1/2.

Energy (cm^{-1})	Energy (K)	g_X	g_Y	g_Z
0	0	1.1589	1.9433	12.8273
11	16	2.5536	5.0093	10.8047
75	108	0.0925	0.9408	14.8139
107	154	3.8681	5.2266	6.8649
153	220	0.8925	2.2511	11.3410
221	318	2.2093	3.9018	7.1324
249	358	0.1832	1.6058	12.5779
320	460	2.0263	4.1820	13.1596