SUPPORTING INFORMATION FOR

Effect of Second Sphere Interactions on the Magnetic Anisotropy of Lanthanide Single-Molecule Magnets: Electrostatic Interactions and Supramolecular Contacts

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Table S1. Crystal data and structure refinement details for **1** and **2**.

	1	**2**
Chemical formula	$[Dy(N\text{-}NCS)_3(H_2O)_5]\cdot 0.45(KSCN)(18C6)$	$[Dy(NO_3)_2(N\text{-}NCS)_3(H_2O)]\cdot(H_2O)\ (NH_4)_2\ 2(18C6)$
M_r	1449.57	1059.50
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, $Pmn2_1$
Temperature (K)	293	293
***a*, *b*, *c* (Å)**	10.1936(7), 10.6025(6), 14.6812(9)	23.783(10), 11.337(5), 8.490(4)
α, β, γ (°)	88.189(3), 79.328(3), 77.725(3)	90, 90, 90
***V* (Å^3)**	1523.57(17)	2289.1(17)
Z	1	2
Radiation type	Mo K_α	Mo K_α
μ (mm^{-1})	2.80	1.85
Crystal size (mm)	0.42 × 0.11 × 0.08	0.20 × 0.14 × 0.13
T_{min}, T_{max}	0.448, 0.746	0.621, 0.925
No. of measured, independent and observed [I > 2σ(I)] reflections	11590, 5966, 4859	17432, 4602, 4197
R_{int}	0.049	0.062
(sin θ/λ)$_{max}$ (Å^{-1})	0.617	0.617
Refinemen		
R*[*F*^{2} > 2s(*F*^{2})], *wR*(*F*^{2}), *S	0.056, 0.149, 1.07	0.033, 0.068, 1.03
No. of reflections	5966	4602
No. of parameters	343	288
No. of restraints	1	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	1.57, -1.33	0.67, -0.72

Table S2. Selected bond distances (Å) and angles (°) for **1**, and **2**

		1	
Dy1—O2w	2.369(6)	Dy1—O1w	2.391(5)
Dy1—N1	2.371(7)	Dy1—N2	2.421(8)
Dy1—O3w	2.372(7)	Dy1—O4w	2.440(6)
Dy1—O5w	2.382(6)	Dy1—N3	2.389(7)
O2w—Dy1—N1	81.4(3)	N3—Dy1—O1w	73.6(2)
O2w—Dy1—O3w	76.8(3)	O2w—Dy1—N2	147.2(2)
N1—Dy1—O3w	74.1(3)	N1—Dy1—N2	75.8(3)
O2w—Dy1—O5w	140.8(2)	O3w—Dy1—N2	118.0(3)
N1—Dy1—O5w	115.9(3)	O5w—Dy1—N2	71.5(2)
O3w—Dy1—O5w	75.3(2)	N3—Dy1—N2	79.3(3)
O2w—Dy1—N3	106.5(3)	O1w—Dy1—N2	80.0(2)
N1—Dy1—N3	142.2(3)	O2w—Dy1—O4w	73.6(2)
O3w—Dy1—N3	143.5(3)	N1—Dy1—O4w	142.5(3)
O5w—Dy1—N3	81.5(3)	O3w—Dy1—O4w	73.4(3)
O2w—Dy1—O1w	71.3(2)	O5w—Dy1—O4w	72.5(2)
N1—Dy1—O1w	74.4(3)	N3—Dy1—O4w	73.0(2)
O3w—Dy1—O1w	137.7(2)	O1w—Dy1—O4w	121.0(2)
O5w—Dy1—O1w	145.0(2)	N2—Dy1—O4w	137.1(2)
		2	
Dy1—N3	2.363(6)	Dy1—O7	2.410(6)
Dy1—N3^{i}	2.363(6)	Dy1—O17	2.483(10)
Dy1—N4	2.369(6)	Dy1—O8^{i}	2.500(4)
Dy1—O1	2.377(9)	Dy1—O8	2.500(4)
N3—Dy1—N3^{i}	154.5(3)	O7—Dy1—O17	52.7(3)
N3—Dy1—N4	82.12(15)	N3—Dy1—O8^{i}	127.19(17)
N3^{i}—Dy1—N4	82.12(15)	N3^{i}—Dy1—O8^{i}	76.42(17)
N3—Dy1—O1	97.92(15)	N4—Dy1—O8^{i}	141.6(2)
N3^{i}—Dy1—O1	97.92(15)	O1—Dy1—O8^{i}	74.9(3)
N4—Dy1—O1	77.1(4)	O7—Dy1—O8^{i}	76.60(18)
N3—Dy1—O7	88.46(14)	O17—Dy1—O8^{i}	123.6(2)
N3^{i}—Dy1—O7	88.46(14)	N3—Dy1—O8	76.42(17)
N4—Dy1—O7	134.6(4)	N3^{i}—Dy1—O8	127.19(17)
O1—Dy1—O7	148.3(3)	N4—Dy1—O8	141.6(2)
N3—Dy1—O17	79.02(14)	O1—Dy1—O8	74.9(3)
N3^{i}—Dy1—O17	79.02(14)	O7—Dy1—O8	76.60(18)
N4—Dy1—O17	81.9(4)	O17—Dy1—O8	123.6(2)
O1—Dy1—O17	158.9(2)	O8^{i}—Dy1—O8	51.0(2)

Symmetry codes: i: -*x*, *y*, *z*. ii: *x*, -*y* + ½, *z*.

Table S3. Hydrogen-bond geometry (Å, °) for **2**

D—H···A	**D—H**	**H···A**	**D···A**	**D—H···A**
		2		
O1—H1w···O7w^{iii}	0.85	1.88	2.694(13)	159

Symmetry codes: iii: *x*, *y* - 1, *z*; iv: x, *y* - 1, *z* - 1; v: -*x* + 1, -*y* + 1, -*z* + 1.

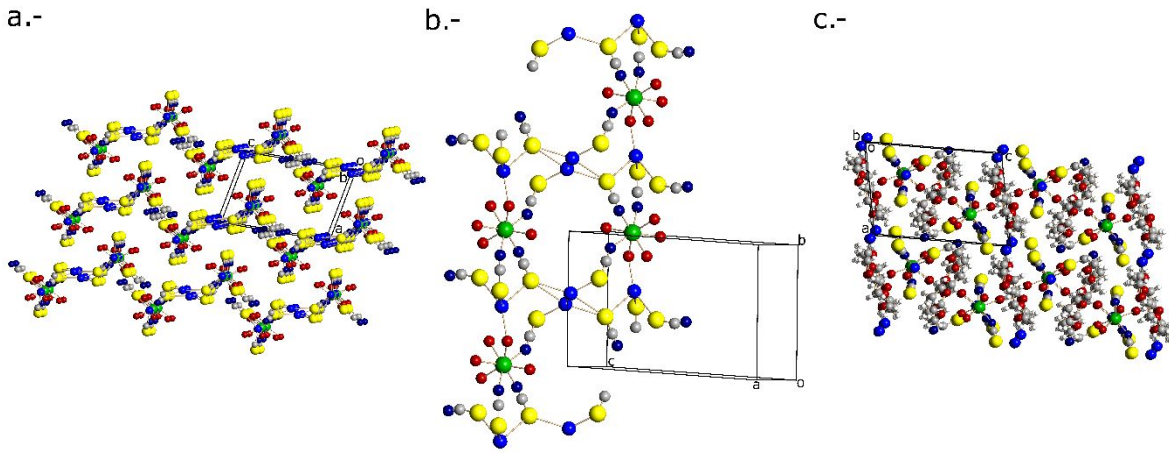


Figure S1. Packing view for the structure of [Dy(*N*-NCS)$_3$(H$_2$O)$_5$]· 0.45(KNCS)·(18-crown-6). **a.-** View along [010] and crown ether molecules omitted. **b.-** Approximately [100] view of chains defined by [Dy(*N*-NCS)$_3$(H$_2$O)$_5$] units and the interstitial potassium ions. **c.-** View along [010].

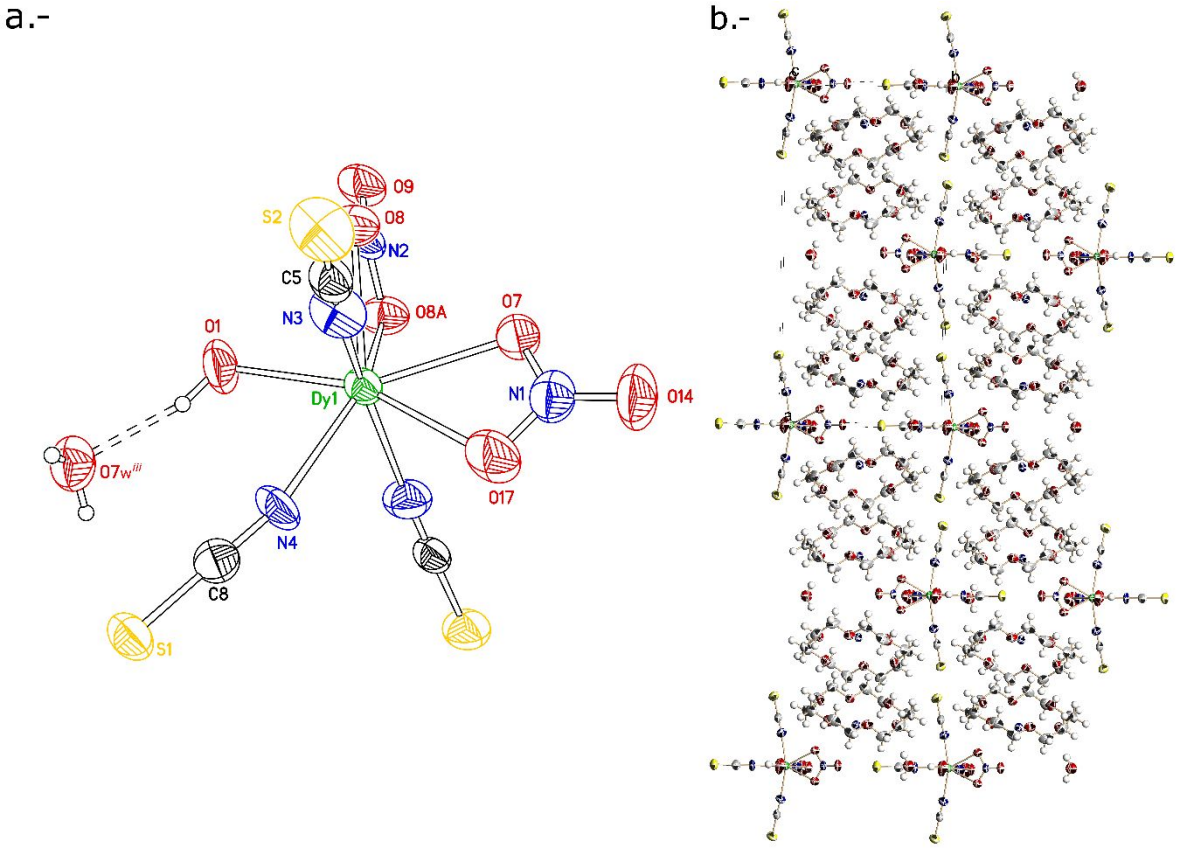


Figure S2. a.- Hydrogen bond between [Dy(NO$_3$)$_2$(-*N*-NCS)$_3$(H$_2$O)]$^{2-}$ (**2**) and the crystallization water. **b.-** Packing view along [001].

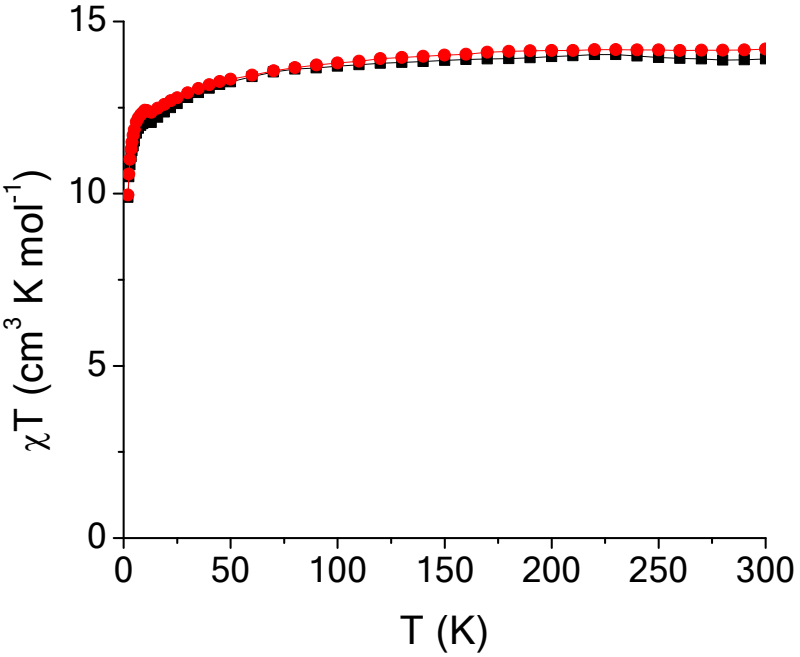


Figure S3. Temperature dependent magnetic susceptibility for **1** (black), **2** (red) at a static field of 3000Oe.

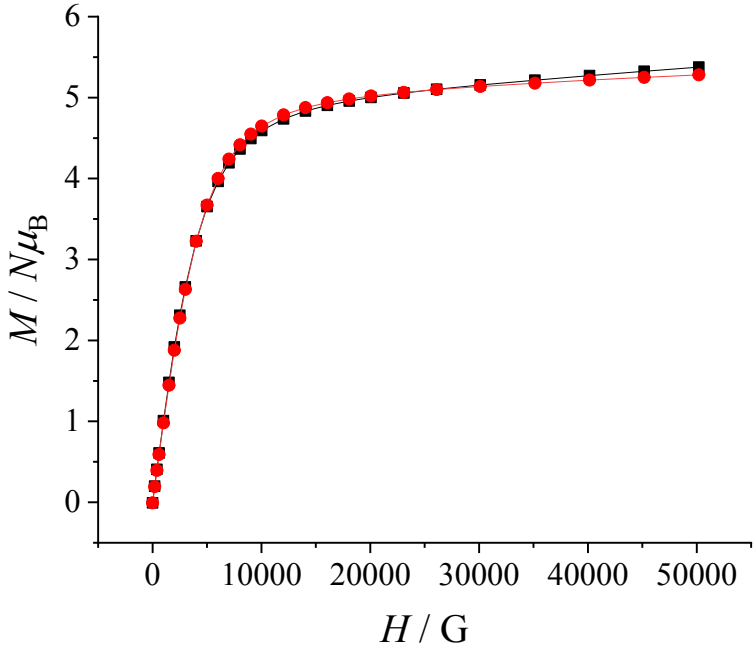


Figure S4. Field dependence of the magnetization measured at 2 K for **1** (black) and **2** (red).

Table S4. Natural atomic charges for different fragments of the 'full' and 'small' models of **1** and **3**.

	1			**3**	
	full	small		full	small
Y	1.976	1.971	Y	1.848	1.856
SCN	-0.839	-0.829	NO_3	-0.736	-0.737
SCN	-0.830	-0.824	NO_3	-0.735	-0.733
SCN	-0.833	-0.827	NO_3	-0.741	-0.732
H_2O	0.082	0.103	H_2O (W1)	0.080	0.116
H_2O	0.084	0.096	H_2O (W2)	0.063	0.113
H_2O	0.081	0.102	H_2O (W3)	0.080	0.116
H_2O	0.087	0.106			
H_2O	0.083	0.101			
2 $C_{12}O_6H_{24}$	0.108	-	2 $C_{12}O_6H_{24}$	0.141	-

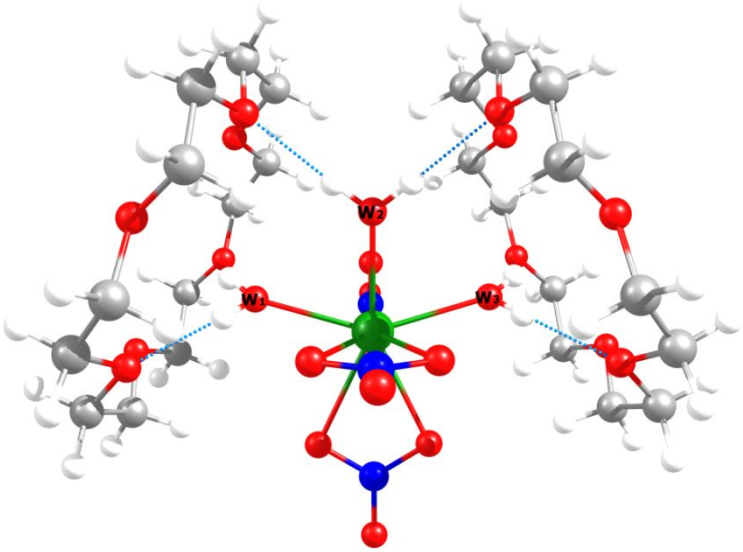
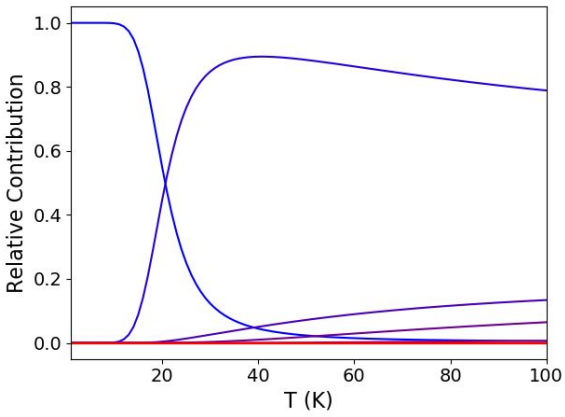
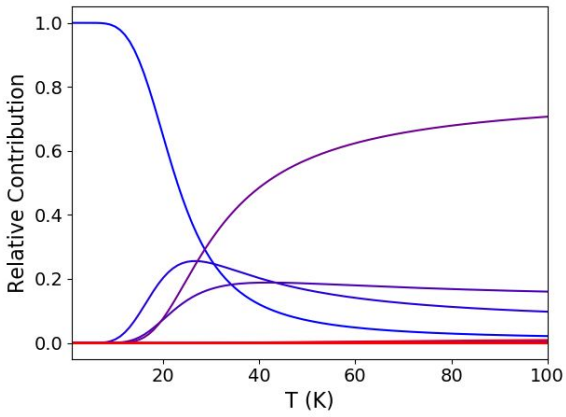


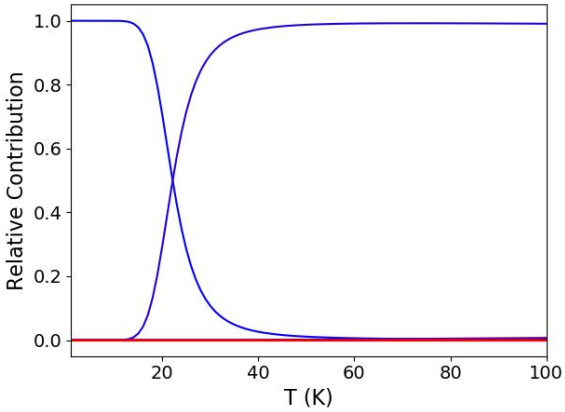
Figure S5. Hydrogen bonds between water ligands coordinated in complex **3** with crown ether molecules. Water molecules are labelled according to Table S4



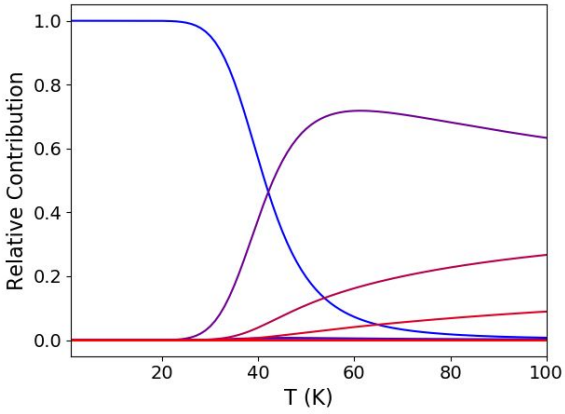
1 ‘small’



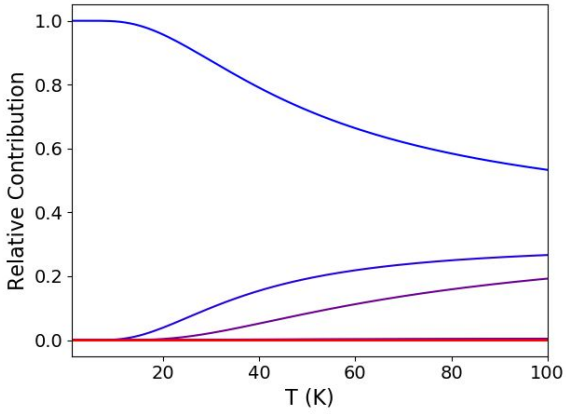
1 ‘large’



2



3 ‘small’



3 ‘large’

Figure S6. Contribution of the first eight Kramers’ doublets to tunnelling demagnetization for **1**, **2** and **3**. First to eighth doublets are depicted in a color scale from blue to red.

Table S5. Parameters fitted from Cole-Cole plots for **1** and **2**.

Molecule	T	$\chi_{s,tot}$	$\Delta\chi_1$	τ_1	α_1	$\Delta\chi_2$	τ_2	α_2
1	1.8	-0.1769	5.7989	2.07E-03	0.6538	0.6121	0.1582	0.0621
	1.9	-0.2821	5.7664	2.01E-03	0.6810	0.7362	0.1513	0.1320
	2.0	-0.1670	5.6243	2.60E-03	0.6851	0.6155	0.1384	0.1454
	2.1	-0.1105	5.3848	2.69E-03	0.6865	0.5942	0.1281	0.1428
	2.3	-0.0341	5.3608	3.63E-03	0.6899	0.3691	0.1837	0.1838
	2.5	0.1991	4.4938	2.69E-03	0.6503			
	2.7	0.2919	4.1370	2.52E-03	0.6339			
	3.0	0.4220	3.5801	2.13E-03	0.6022			
	3.3	0.4802	3.2126	1.70E-03	0.5836			
	3.6	0.5421	2.8549	1.37E-03	0.5730			
	4.0	0.7519	2.2941	1.29E-03	0.5312			
	4.5	0.9894	1.6816	1.25E-03	0.4263			
	5.0	1.0259	1.3677	7.74E-04	0.3378			
	5.5	1.0062	1.1741	3.94E-04	0.2800			
	6.0	0.9907	0.9713	1.78E-04	0.2150			
	6.5	0.8385	0.9922	6.77E-05	0.2484			
	7.0	1.1508	0.5533	7.22E-05	0.0798			
	7.5	1.0570	0.5487	3.19E-05	0.0515			
2	1.8	0.2991	7.5660	4.86E-01	0.3397			
	1.9	0.2856	7.3697	4.62E-01	0.3401			
	2.1	0.2624	6.7326	3.83E-01	0.3371			
	2.4	0.2431	5.6485	2.38E-01	0.3063			
	2.7	0.2333	4.7095	1.36E-01	0.2615			
	3.0	0.2252	3.9866	7.74E-02	0.2115			
	3.3	0.2140	3.4994	4.66E-02	0.1740			
	3.6	0.2022	3.1561	2.93E-02	0.1466			
	3.9	0.1902	2.8988	1.90E-02	0.1275			
	4.2	0.1792	2.6946	1.26E-02	0.1163			
	4.5	0.1693	2.5186	8.58E-03	0.1067			
	5.0	0.1574	2.2783	4.62E-03	0.0972			
	5.5	0.1514	2.0749	2.55E-03	0.0889			
	6.0	0.1513	1.8985	1.44E-03	0.0806			
	6.5	0.1536	1.7455	8.37E-04	0.0738			
	7.0	0.1565	1.6133	4.95E-04	0.0683			
	8.0	0.1605	1.3982	1.85E-04	0.0621			
	9.0	0.2252	1.1664	8.07E-05	0.0492			
	10.0	0.4332	0.8246	4.78E-05	0.0238			
	11.0	0.5288	0.6188	2.72E-05	0.0233			