

Electronic Supplementary Information

Synthesis, structural characterization and magnetic behaviour of a butterfly $[\text{Co}_2^{\text{III}}\text{Ln}_2^{\text{III}}]$ compounds family

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Table ESI1. Main bond angles ($^{\circ}$) and distances (\AA) of **1-5**.

	1	2	3	4	5
Ln1-O12	2.379(3)	2.360(3)	2.362(3)	2.339(2)	2.334(2)
Ln1-O13	2.403(3)	2.455(5)	2.376(4)	2.436(3)	2.338(4)
Ln1-O14	2.269(3)	2.253(3)	2.245(4)	2.226(2)	2.211(3)
Ln1-O15	2.451(2)	2.446(4)	2.442(4)	2.420(3)	2.407(3)
Ln1-O15_a	2.457(2)	2.454(3)	2.443(3)	2.434(2)	2.419(2)
Ln1-O21	2.359(3)	2.372(3)	2.336(3)	2.327(2)	2.313(3)
Ln1-O23	2.460(3)	2.389(4)	2.451(5)	2.361(3)	2.418(3)
Ln1-O24	2.273(2)	2.261(4)	2.239(3)	2.231(3)	2.206(2)
Co2-N14	1.991(4)	1.990(4)	1.984(5)	1.984(4)	1.985(3)
Co2-O11	1.913(2)	1.907(3)	1.917(3)	1.912(2)	1.911(2)
Co2-O14	1.882(2)	1.892(4)	1.884(3)	1.890(2)	1.877(2)
Co2-O15	1.936(2)	1.935(4)	1.932(4)	1.931(3)	1.931(2)
Co2-O22	1.909(2)	1.914(3)	1.915(3)	1.912(2)	1.905(3)
Co2-O24	1.885(2)	1.881(3)	1.893(4)	1.882(2)	1.889(2)
Ln1-Ln1_b	8.298(1)	8.3012(4)	8.3179(5)	8.290(3)	8.360(3)
Ln1-O15-Ln1_a	113.58(9)	113.5(1)	113.4(1)	113.90(9)	113.70(9)
Ln1_a-O14-Co2	105.0(1)	104.4(2)	105.0(2)	103.8(1)	104.9(1)
Ln1-O15-Co2	96.96(9)	96.6(1)	96.0(1)	96.43(9)	95.82(9)
Ln1_a-O15-Co2	96.76(9)	96.4(1)	96.6(1)	95.89(9)	95.87(9)
Ln1-O24-Co2	104.8(1)	105.0(2)	104.2(2)	105.1(1)	104.1(1)
Ln1-Co2-Ln1_a	76.88(1)	77.05(2)	77.11(2)	77.24(1)	77.14(1)
Co2-Ln1-Co2_a	103.12(1)	102.95(2)	102.89(2)	102.76 (1)	102.86 (1)

Symmetry code: (a) 1-x, -y, 2-z ; (b) -x, -y, 2-z

Table ESI2. Main bond angles (°) and distances (Å) of **6**.

Distances (Å)		Angles (°)	
6		6	
Gd1-O1	2.385(3)	Gd1-O7-Gd1_a	114.7(1)
Gd1-O3	2.284(3)	Gd1-O3-Co4	106.1(1)
Gd1-O7	2.515(3)	Gd1-O4_a-Co4_a	104.5(1)
Gd1-O9	2.381(5)	Gd1-O7-Co4	96.3(1)
Gd1-O11	2.477(3)	Gd1_a-O7-Co4	97.7(1)
Gd2-O12	2.305(3)	Gd2-O16-Gd2_b	114.5(1)
Gd2-O16	2.530(3)	Gd2-O12-Co3	106.2(1)
Gd2-O17	2.474(5)	Gd2_b-O13-Co3	104.7(1)
Gd2-O18	2.365(3)	Gd2-O16-Co3	96.4(1)
Gd2-O21	2.374(4)	Gd2_b-O16-Co3	97.5(1)
Co3-N2	2.002(4)	Gd1-Co4-Gd1-a	78.05(2)
Co3-O12	1.875(3)	Co4-Gd1-Co4_a	101.95(2)
Co3-O13	1.884(4)	Gd2-Co3-Gd2_b	77.94(2)
Co3-O14	1.912(3)	Co3-Gd2-Co3_b	102.06(2)
Co3-O16	1.935(3)		
Co3-O20	1.922(4)		
Co4-N1	1.988(5)		
Co4-O2	1.927(3)		
Co4-O3	1.877(3)		
Co4-O4	1.884(3)		
Co4-O6	1.908(3)		
Co4-O7	1.934(3)		
Gd1-Gd1_a	4.200(6)		
Gd2-Gd2_b	4.2017(6)		

Symmetry code: (a) 1-x, -y, -z ; (b) 1-x, 1-y, -1-z ; (c) 2-x, -y, -z

Table ESI3. Intra-molecular and closest Ln ⋯ Ln inter-molecular distances (Å) of **1-6**.

	1	2	3	4	5	6
Ln-Ln (intra)	4.1061(6)	4.0970(4)	4.0840(4)	4.069(1)	4.041(1)	4.200(6)/4.2017(6)

Ln-Ln (inter) 8.298(1) 8.3012(4) 8.3179(5) 8.290(3) 8.360(3) 9.387(1)/9.698(1)

Figure ESI1. Molecule representation of complex 5. H atoms omitted for sake of clarity.

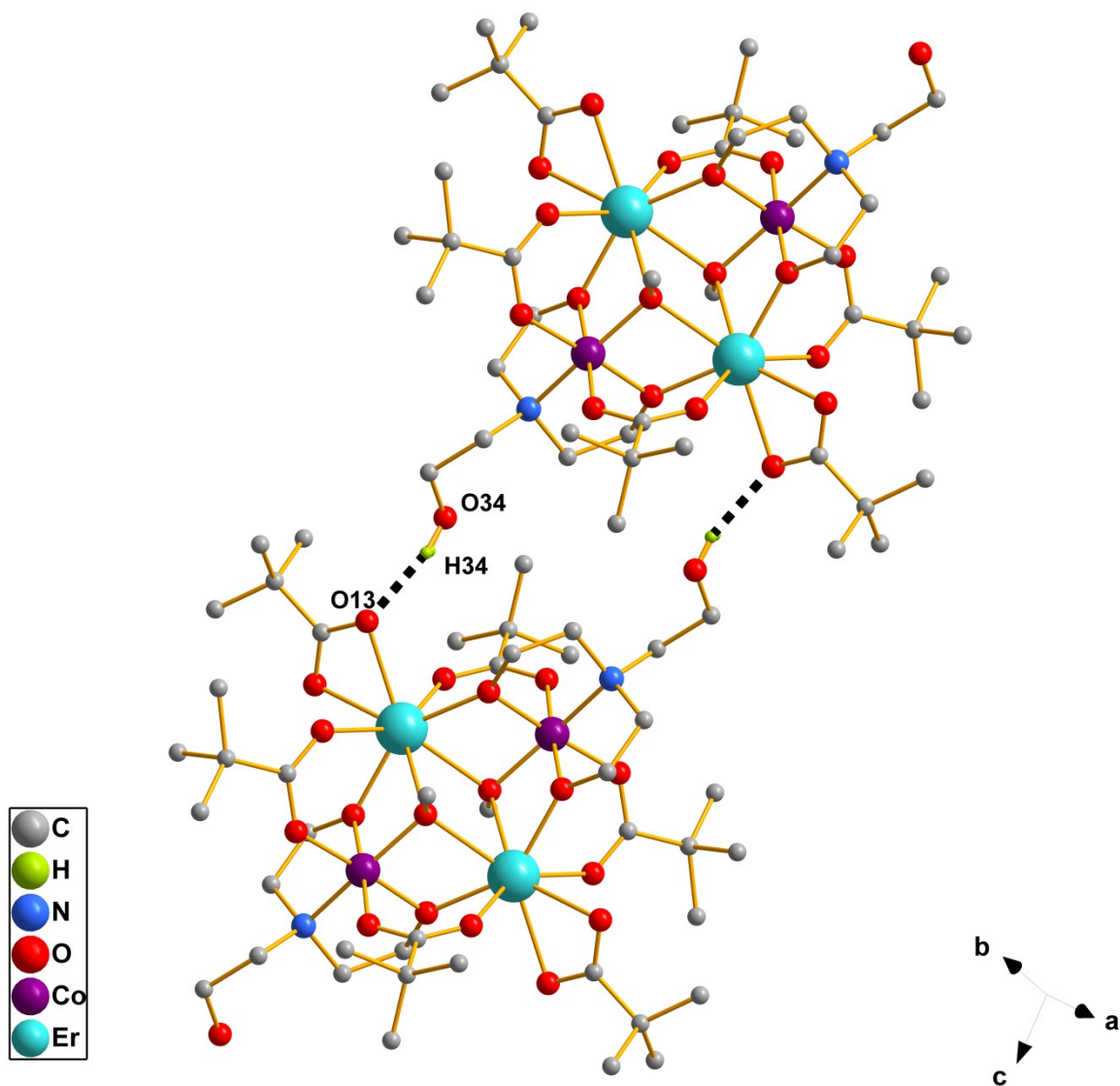


Figure ESI2. Ball and stick molecular representation of complex 5 structure highlighting the inter-molecular H-bond interactions. H atoms omitted for sake of clarity

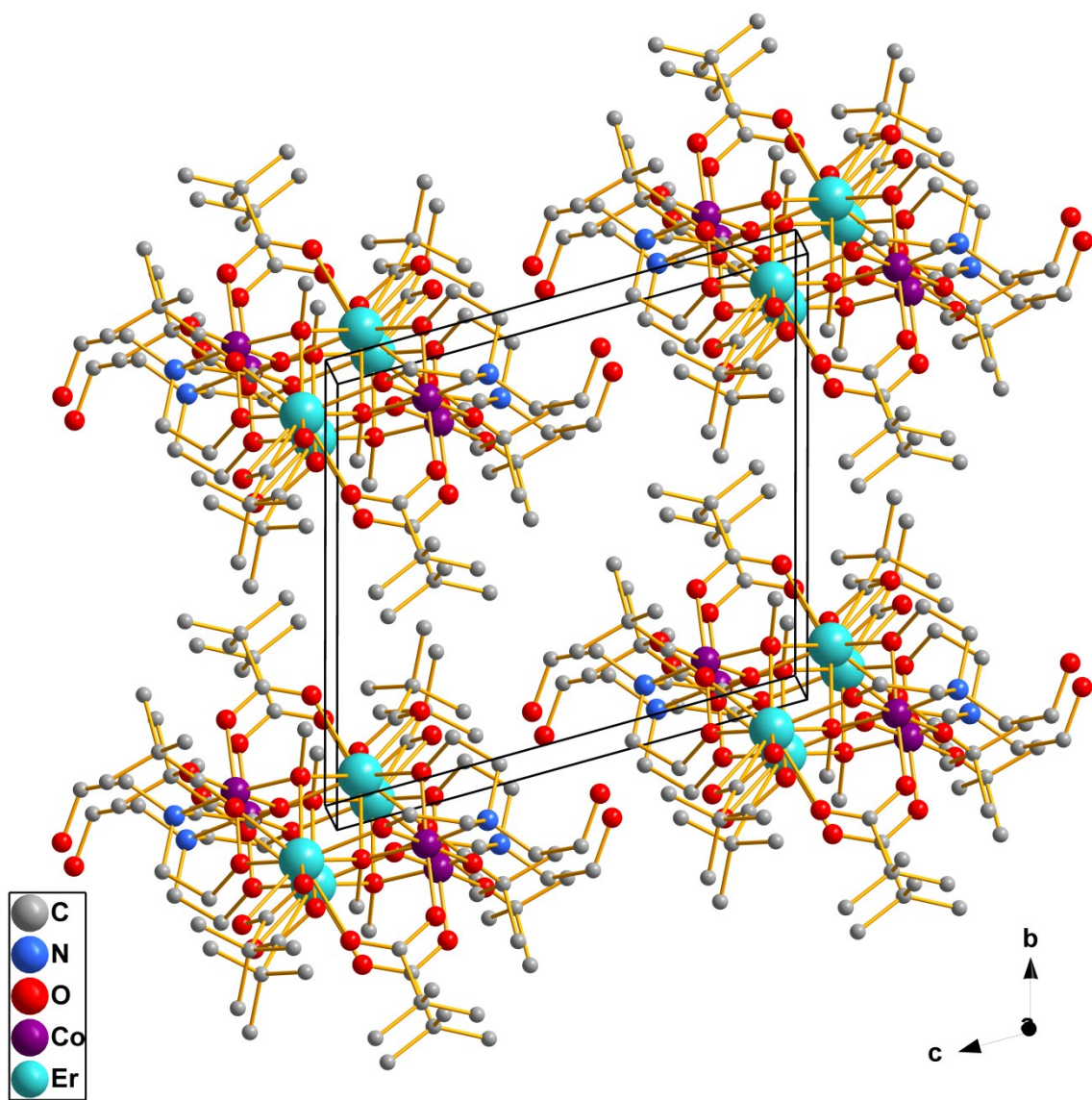


Figure ESI3. Ball and stick molecular representation of complex **5** crystal packing. View along a - axis.

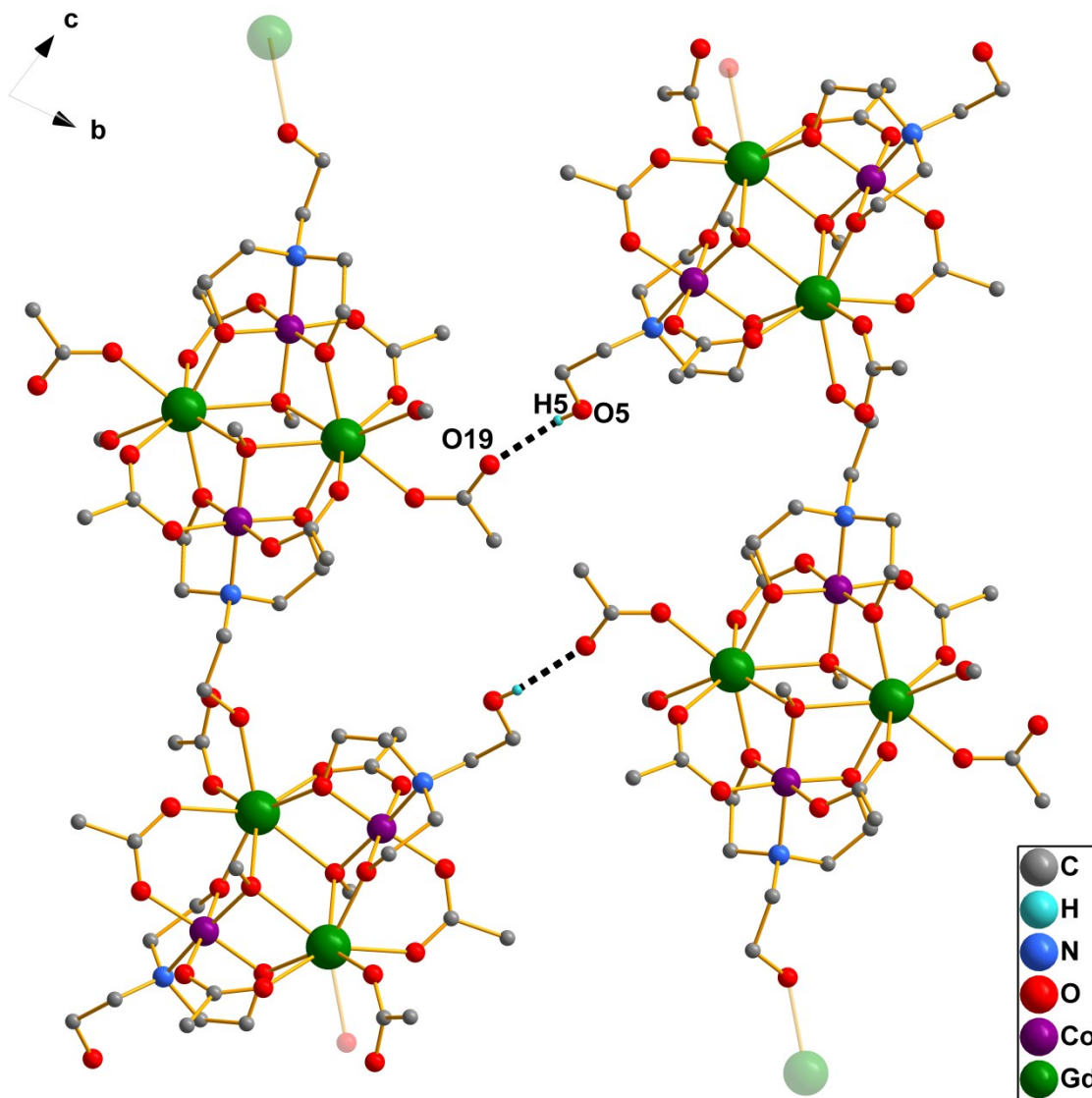


Figure ESI4. Ball and stick molecular representation of complex **6** structure highlighting the inter-molecular H-bond interactions between chains. H atoms omitted for sake of clarity.

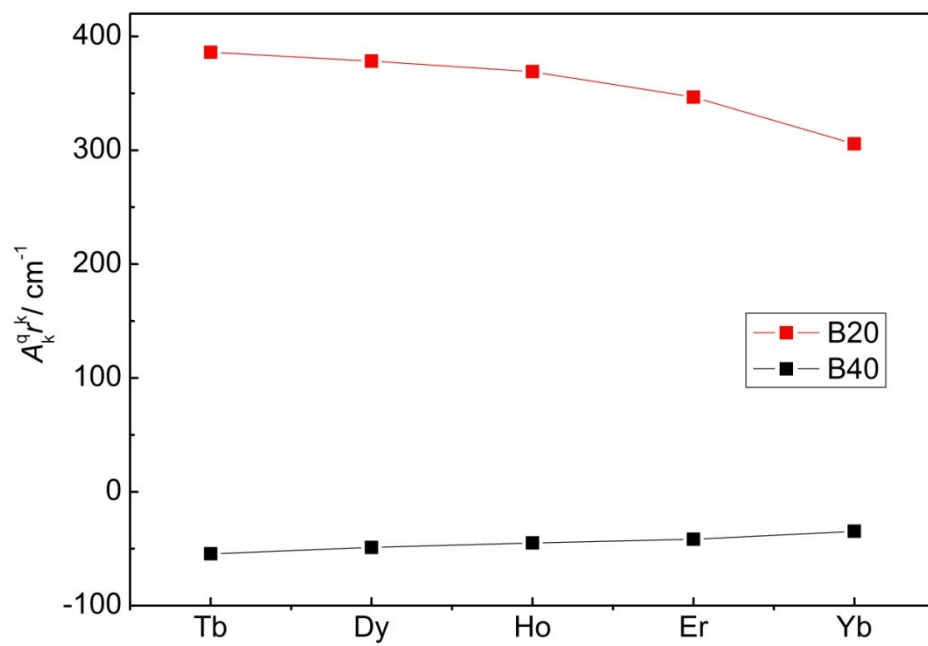


Figure ES15. Correlation of best fitting crystal field parameters, $A_2^0 \langle r^2 \rangle$ and $A_4^0 \langle r^4 \rangle$ with increasing Ln(III) Z number.

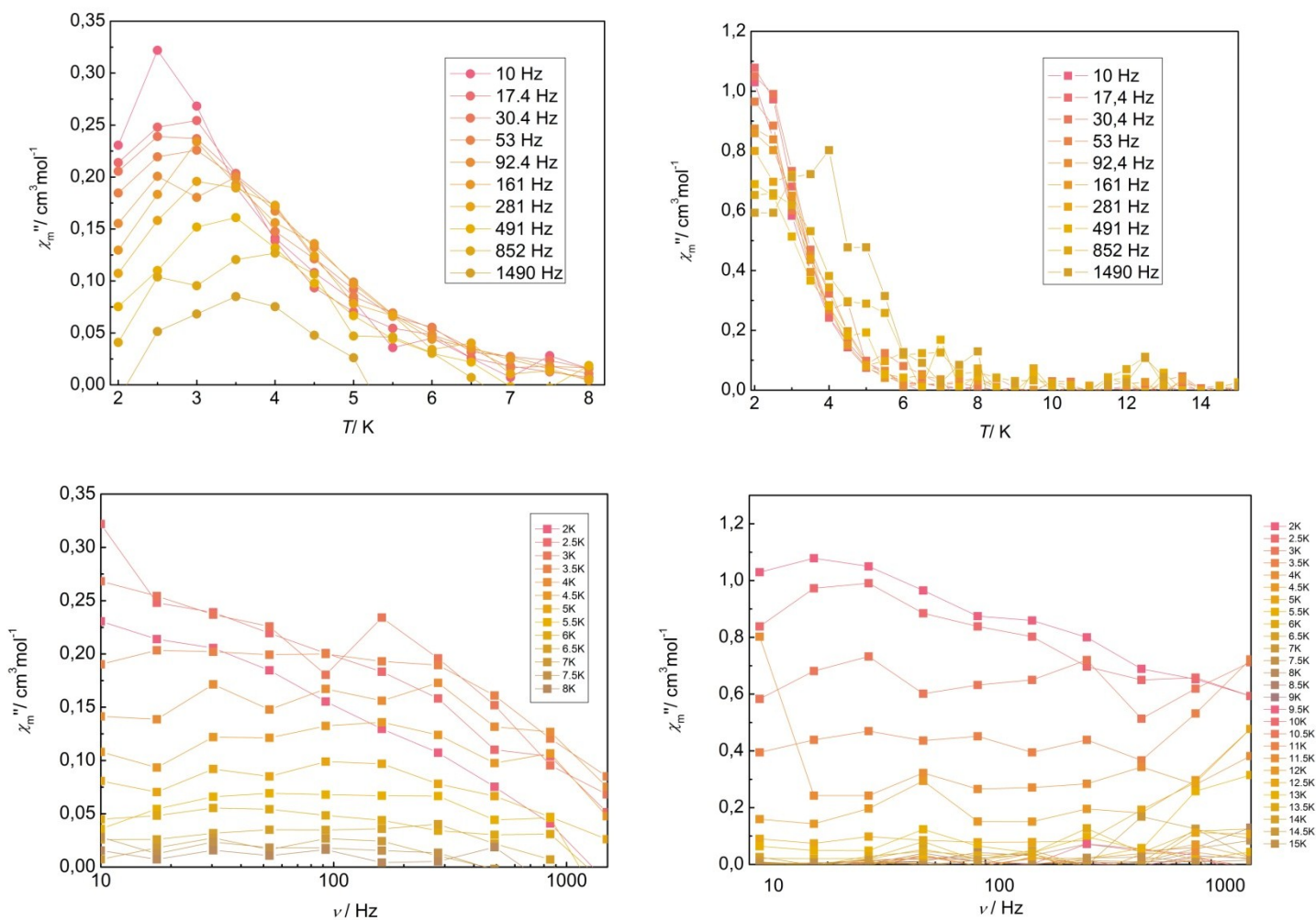
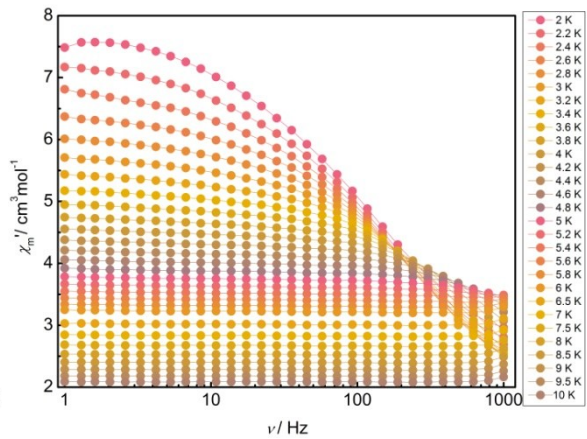
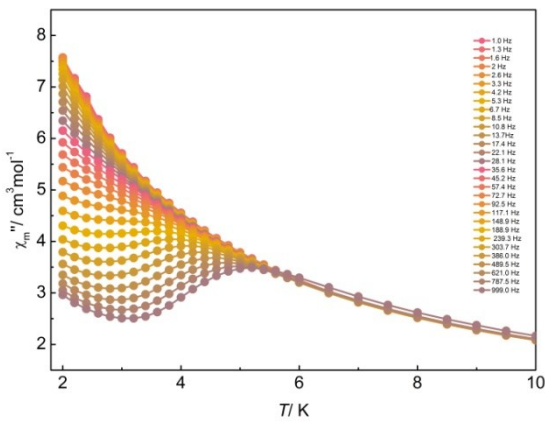
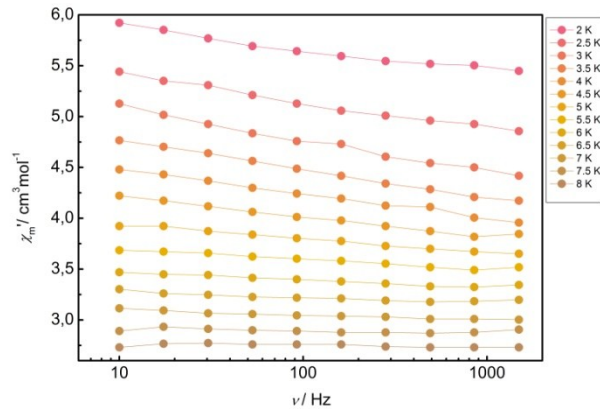
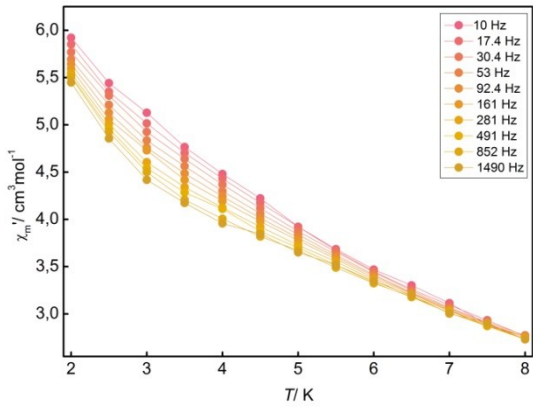
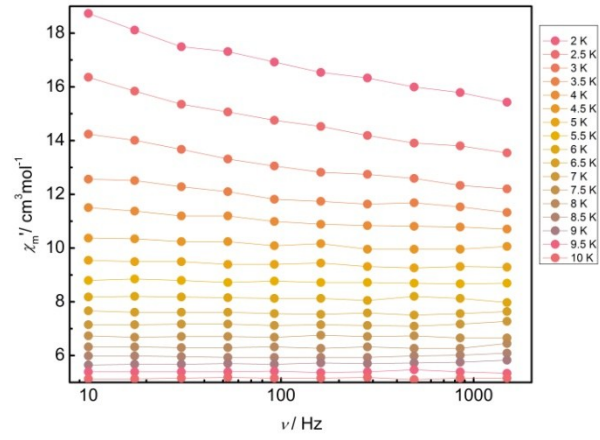
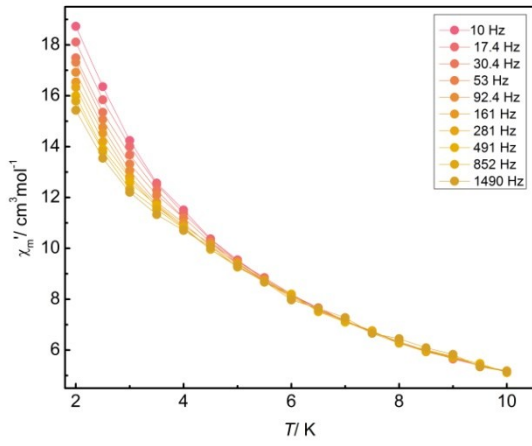


Figure ESI6. Temperature (top) and frequency (bottom) AC out of phase susceptibility data dependence of complexes **1**, Tb (right) and **3**, Ho (left) under 1 and 3 kOe DC applied field respectively. Full lines are just for eyes guiding. Frequency dependence plot is shown in logarithmic scale.



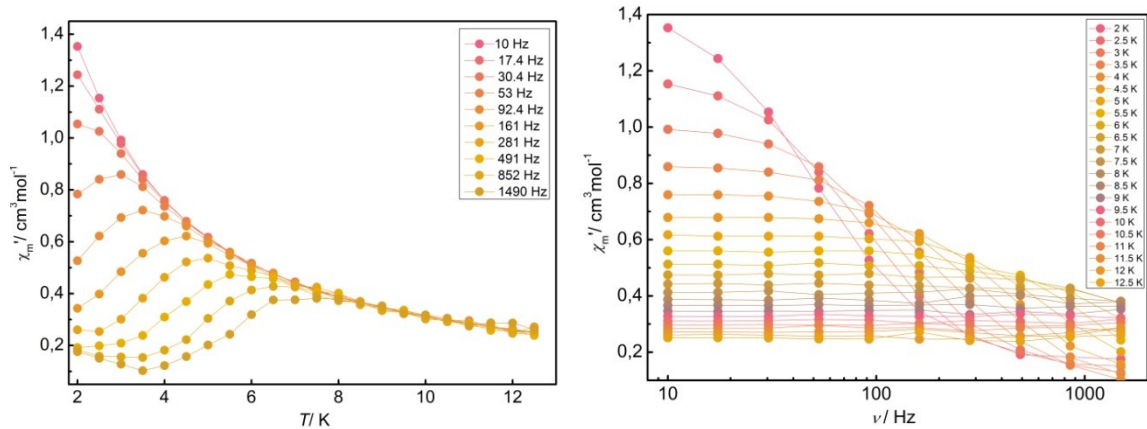


Figure ESI7. Temperature (left) and frequency (right) AC in phase susceptibility data dependence of complexes **1** (Tb), **3**, (Ho), **4**(Er) and **5** (Yb) (top to bottom) under DC applied field. Full lines are just for eyes guiding. Frequency dependence plot is shown in logarithmic scale.

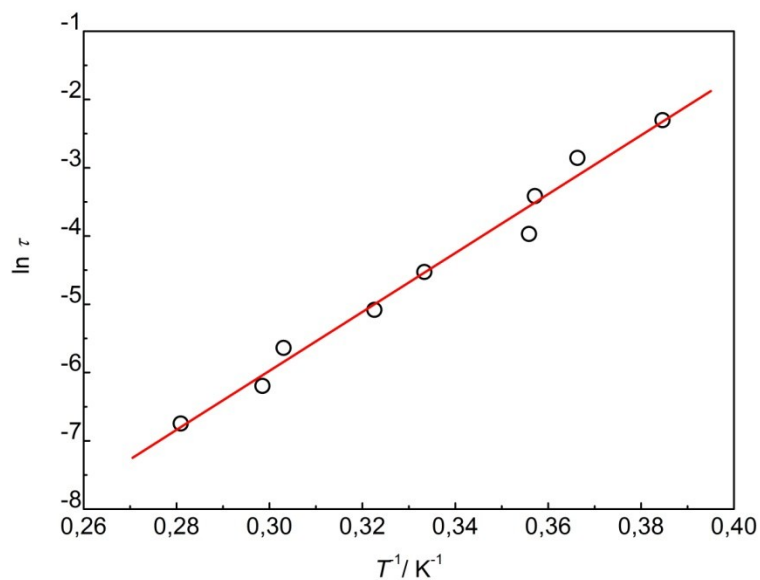


Figure ESI8. Temperature dependence of characteristic magnetization relaxation times as $\ln \tau$ vs. T^{-1} plots of complex **3**, Ho. Full line: best fitting plot, see text.

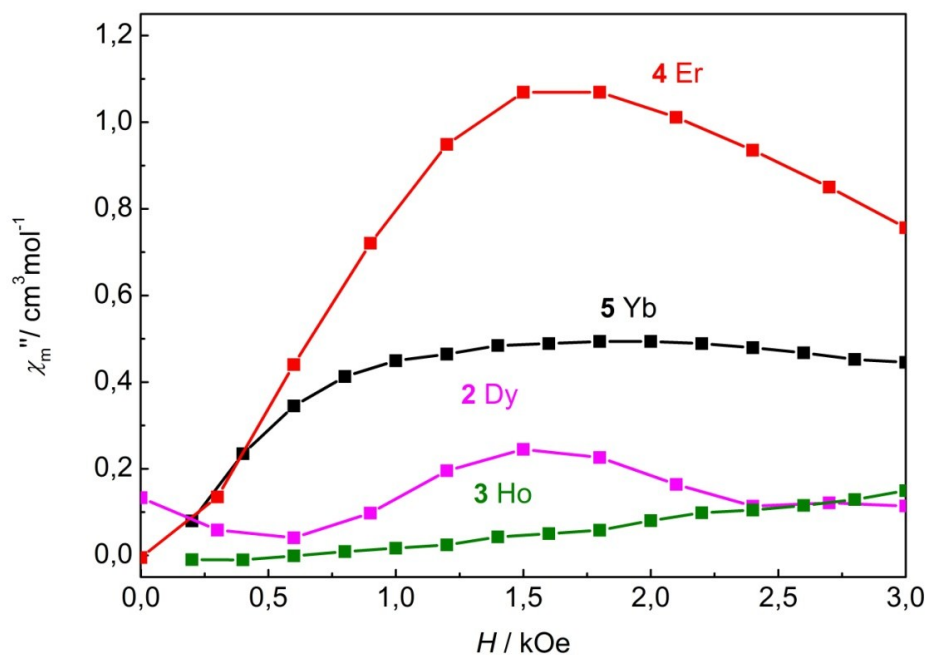
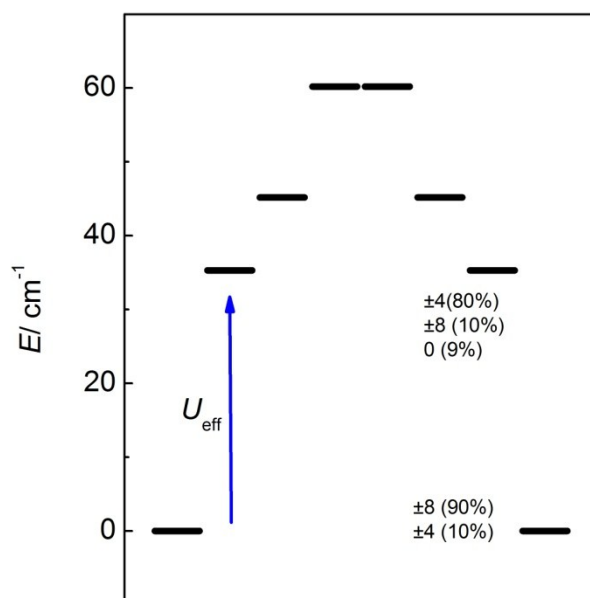


Figure ESI9. Out of phase susceptibility response at 2K with 100 Hz AC frequency under DC applied fields in the range 0-3 kOe for complexes **1-5**. Lines are just as eyes-guideline.



Figure

ESI10. Crystal

field low lying energy level splitting of $J=8$ manifold as arising from DC data fitting of Ho complex **3**.

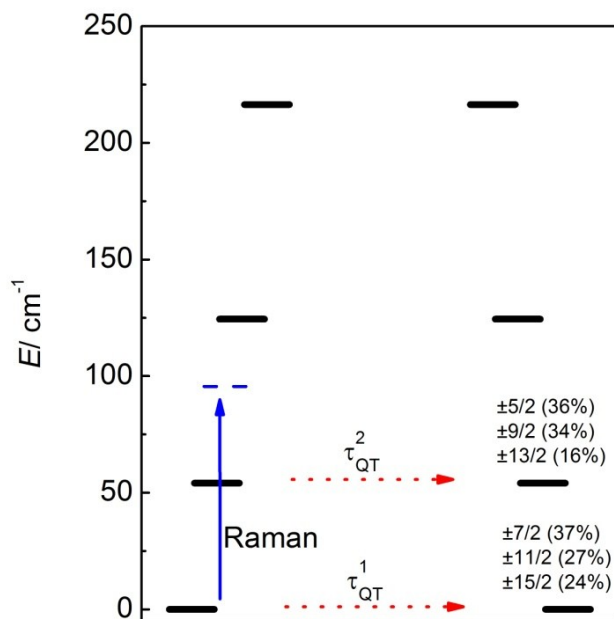


Figure ESI11. Crystal field low lying energy level splitting of $J=15/2$ manifold as arising from DC data fitting of Er complex **4**.

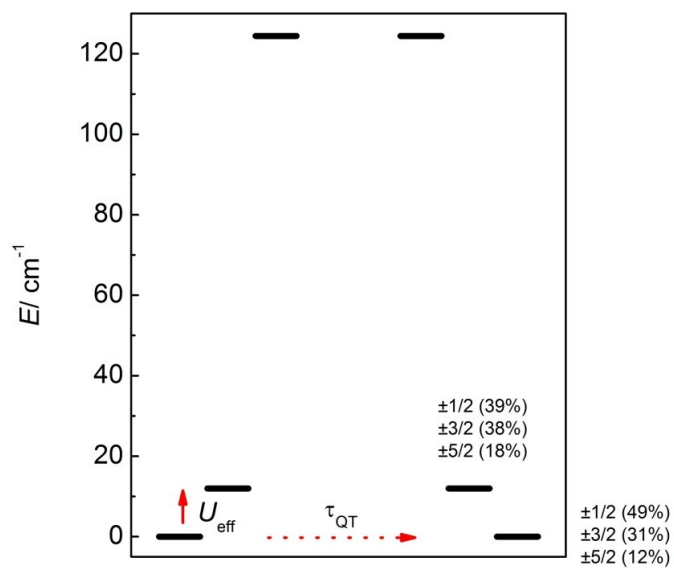


Figure ESI12. Crystal field low lying energy level splitting of $J=7/2$ manifold as arising from DC data fitting of Yb complex **5**.