Towards comparative investigation of Er- and Yb-based SMMs: the effect of coordination environment configuration on the magnetic relaxation in the series of heteroleptic thiocyanate complexes

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We prepared and studied two similar series of Er and Yb thiocyanates, involving $[Ln(H_2O)_5(NCS)_3]\cdot H_2O$ (**1Er**, **1Yb**) as well as the molecular and ionic complexes with 2,2'-bipyridine (bpy) and 1,10-phenantroline (phen), $[Ln(H_2O)(bpy)_2(NCS)_3]\cdot 0.5(bpy)\cdot H_2O$ (**2Er**, **2Yb**), $[Ln(H_2O)(phen)_2(NCS)_3]\cdot phen\cdot 0.5H_2O$ (**3Er**, **3Yb**), $[Hbpy][Ln(bpy)_2(NCS)_4]\cdot H_2O$ (**4Er**, **4Yb**) and $[Hphen][Ln(phen)_2(NCS)_4]$ (**5Er**, **5Yb**). All the complexes were found to exhibit the properties of field-induced single-molecule magnets. For **1Yb**, the effective value of the energy barrier for magnetization reversal, Δ_{eff}/k_B, equals to 50 K, which is among the highest ones currently known for molecular SMMs on the basis of Yb^{3+}. The obtained data are discussed involving essential structural features of the complexes, namely the configuration of the Ln environment, i.e. its composition, geometry as well as mutual distribution of different donating centers. To the best of our knowledge, this work also involves experimental investigation of the largest and thus sufficiently representative series of similar mononuclear SMMs on the basis of Er and Yb within one study.

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Contents

Table S1. Crystal data and structure refinement for the complexes.

Identification code	**1Er**	**1Yb**
Empirical formula	$C_3H_{12}ErN_3O_6S_3$	$C_3H_{12}N_3O_6S_3Yb$
Formula weight	449.60	455.38
Temperature, K	120(2)	120(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a, Å	8.4333(2)	8.4131(3)
b, Å	7.1468(2)	7.1324(3)
c, Å	12.2023(3)	12.1620(4)
β, °	103.7620(10)	103.8360(10)
Volume, $Å^3$	714.33(3)	708.61(5)
Z	2	2
D (calc), Mg/m^3	2.090	2.134
μ, mm^{-1}	6.325	7.054
F(000)	430	434
Crystal size, mm	0.4 x 0.2 x 0.18	0.4 x 0.2 x 0.18
θ range, °	2.665, 33.122	2.671, 33.146
Index ranges	-12<=h<=12 -10<=k<=10 -18<=l<=18	-12<=h<=12 -10<=k<=10 -18<=l<=18
Reflections collected	15215	14999
Independent reflections, Rint	5136, 0.0213	5103, 0.0220
Completeness to θ = 25.242°	99.9 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max,. min. transmission	0.2693, 0.1539	0.2693, 0.1826
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5136 / 13 / 183	5103 / 13 / 183
Goodness-of-fit	1.042	1.212
R1, wR2 [I>2sigma(I)]	0.0276, 0.0696	0.0280, 0.0694
R1, wR2 (all data)	0.0291, 0.0710	0.0295, 0.0704
Absolute structure parameter	0.057(17)	0.398(17)
Largest diff. peak and hole, $e.Å^{-3}$	0.551, -0.804	0.582, -0.858

2Er

File 1 : S:\Andr\Paper\SP_Er_Yb_NCS\Pow\2\Er_NCS_bpy\Er_NCS_bpy_2018_04_26.raw_1

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Range Number :  1
```

R-Values

```
Rexp : 4.10     Rwp : 8.46      Rp  : 6.67   GOF : 2.07
Rexp`: 8.86     Rwp`: 18.30     Rp` : 16.64  DW  : 0.56

Number of independent parameters : 14
```

Quantitative Analysis - Rietveld

```
   Phase 1  : [Er(H2O)(bpy)2(NCS)3]•0.5(bpy)•H2O  100.000 %
```

Background

```
   Chebychev polynomial, Coefficient  0      353.5(14)
                                      1      -44.2(19)
                                      2      -10.5(17)
                                      3      5.7(16)
```

Instrument

Primary radius (mm)	280
Secondary radius (mm)	280
Linear PSD 2Th angular range (°)	2.94
FDS angle (°)	0.8
Beam spill, sample length (mm)	20
Intensity corrected	

Corrections

Specimen displacement	0.22
LP Factor	0

Miscellaneous

Start X	5
Finish X	50

Structure 1

Phase name	[Er(H2O)(bpy)2(NCS)3]•0.5(bpy)•H2O
R-Bragg	4.142
Spacegroup	P-1
Scale	0.00006249(38)
Cell Mass	1536.024
Cell Volume (Å^3)	1538.14(25)
Wt% - Rietveld	100.000
Crystal Linear Absorption Coeff. (1/cm)	72.702(12)
Crystal Density (g/cm^3)	1.65825(26)
Preferred Orientation (Dir 1 : 0 1 -1)	0.4766(40)
(Dir 2 : 0 0 1)	0.7728(66)
Fraction of Dir 1	0.440(10)
PVII peak type	
FWHM = a + b/Cos(Th) + c Tan(Th)	
a	0.0280922
b	0.002285158
c	0.08668674
Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)	
ma	0
mb	0
mc	0.05322237
Lattice parameters	
a (Å)	9.7717(12)
b (Å)	12.98653(96)
c (Å)	13.15957(74)
alpha (°)	110.9886(52)
beta (°)	94.3831(80)
gamma (°)	96.182(11)

Site	Np	x	y	z	Atom	Occ	Beq
Er1	2	0.15487	0.35298	0.16754	Er	1	1
S1	2	0.49312	0.64744	0.47155	S	1	1
S2	2	0.53655	0.20377	-0.04743	S	1	1
S3	2	-0.03347	0.24831	-0.23976	S	1	1
O1	2	0.18500	0.53052	0.15550	O	1	2
H1	2	0.26830	0.57840	0.17880	H	1	4
H2	2	0.13250	0.58000	0.18790	H	1	4
O2	2	0.42460	0.66770	0.21630	O	1	2
H3	2	0.44110	0.70010	0.15740	H	1	4
H4	2	0.47310	0.72220	0.28280	H	1	4
N1	2	0.32790	0.46250	0.31450	N	1	2
N2	2	0.34900	0.33170	0.06650	N	1	2
N3	2	0.05590	0.30030	-0.01950	N	1	2
N4	2	0.26530	0.20290	0.20600	N	1	2
N5	2	-0.00330	0.17030	0.12510	N	1	2
N6	2	0.05360	0.36010	0.34091	N	1	2
N7	2	-0.07820	0.42090	0.18890	N	1	2
N8	2	0.57210	0.89700	0.39650	N	1	2
C1	2	0.39780	0.53890	0.38030	C	1	2

C2	2	0.42720	0.28110	0.01840	C	1	2
C3	2	0.01990	0.27890	-0.11080	C	1	2
C4	2	0.40210	0.21930	0.23800	C	1	2
H4A	2	0.45530	0.28750	0.24430	H	1	4
C5	2	0.46900	0.14060	0.26220	C	1	2
H5A	2	0.56610	0.15450	0.28500	H	1	4
C6	2	0.39200	0.04280	0.25260	C	1	2
H6A	2	0.43510	-0.01300	0.26800	H	1	4
C7	2	0.25240	0.02560	0.22050	C	1	2
H7A	2	0.19780	-0.04210	0.21440	H	1	4
C8	2	0.19040	0.10670	0.19700	C	1	2
C9	2	0.04100	0.09200	0.15900	C	1	2
C10	2	-0.05000	0.00130	0.15540	C	1	2
H10A	2	-0.01730	-0.05270	0.18060	H	1	4
C11	2	-0.18680	-0.01130	0.11600	C	1	2
H11A	2	-0.24970	-0.07310	0.11460	H	1	4
C12	2	-0.23190	0.06600	0.07870	C	1	2
H12A	2	-0.32600	0.05830	0.04910	H	1	4
C13	2	-0.13760	0.15570	0.08500	C	1	2
H13A	2	-0.16910	0.21000	0.05980	H	1	4
C14	2	0.12250	0.33220	0.41680	C	1	2
H14A	2	0.21580	0.31960	0.40910	H	1	4
C15	2	0.06570	0.32090	0.50560	C	1	2
H15A	2	0.11840	0.30130	0.55780	H	1	4
C16	2	-0.06930	0.33880	0.51650	C	1	2
H16A	2	-0.11200	0.33050	0.57620	H	1	4
C17	2	-0.14160	0.36860	0.44070	C	1	2
H17A	2	-0.23500	0.38130	0.44760	H	1	4
C18	2	-0.07830	0.38040	0.35360	C	1	2
C19	2	-0.14810	0.41840	0.27260	C	1	2
C20	2	-0.27670	0.45470	0.28410	C	1	2
H20A	2	-0.32440	0.45250	0.34380	H	1	4
C21	2	-0.33500	0.49390	0.20870	C	1	2
H21A	2	-0.42260	0.51920	0.21610	H	1	4
C22	2	-0.26480	0.49570	0.12300	C	1	2
H22A	2	-0.30280	0.52180	0.06960	H	1	4
C23	2	-0.13770	0.45870	0.11620	C	1	2
H23A	2	-0.08930	0.46000	0.05660	H	1	4
C24	2	0.69470	0.87930	0.35870	C	1	2
H24A	2	0.69860	0.81150	0.29980	H	1	4
C25	2	0.81390	0.95340	0.40040	C	1	2
H25A	2	0.89870	0.93760	0.37160	H	1	4
C26	2	0.80810	1.05060	0.48450	C	1	2
H26A	2	0.88890	1.10440	0.51470	H	1	4
C27	2	0.68360	1.07040	0.52560	C	1	2
H27A	2	0.67800	1.13750	0.58470	H	1	4
C28	2	0.56790	0.99150	0.47970	C	1	2

2Yb

File 1 : H:\SP_Er_Yb_NCS\Pow\2\Yb_NCS_bpy\Yb_NCS_bpy_2018_04_26.raw_1

Range Number : 1

R-Values

Rexp : 2.84 Rwp : 7.84 Rp : 5.91 GOF : 2.76
Rexp`: 5.69 Rwp`: 15.74 Rp` : 12.67 DW : 0.36

Number of independent parameters : 28

Quantitative Analysis - Rietveld

Phase 1 : [Yb(H2O)(bpy)2(NCS)3]•0.5(bpy)•H2O 100.000 %

Background

One on X		860(700)
Chebychev polynomial, Coefficient	0	653(49)
	1	75(55)
	2	-14(30)
	3	-4(17)
	4	26.7(87)
	5	-55.9(57)

Instrument

Primary radius (mm)	280
Secondary radius (mm)	280
Linear PSD 2Th angular range (°)	2.94
FDS angle (°)	1
Beam spill, sample length (mm)	20
Intensity corrected	
Full Axial Convolution	
Filament length (mm)	12
Sample length (mm)	10
Receiving Slit length (mm)	3
Primary Sollers (°)	2.5
Secondary Sollers (°)	2.5

Corrections

Specimen displacement	0.1329832
LP Factor	0

Miscellaneous

Start X	4
Finish X	50

Structure 1

Phase name	[Yb(H2O)(bpy)2(NCS)3]•0.5(bpy)•H2O
R-Bragg	3.414
Spacegroup	P-1
Scale	0.0001581(12)
Cell Mass	1547.582
Cell Volume (Å^3)	1537.65(26)
Wt% - Rietveld	100.000
Crystal Linear Absorption Coeff. (1/cm)	78.648(13)
Crystal Density (g/cm^3)	1.67127(28)
Preferred Orientation Spherical Harmonics	
Order	4
y00	1
y20	0.369(20)
y21m	-0.425(17)
y21p	-0.008(15)
y22m	-0.231(22)
y22p	-0.516(14)
y40	-0.075(25)
y41m	0.280(22)
y41p	0.009(20)
y42m	0.115(20)
y42p	-0.320(16)
y43m	0.322(15)
y43p	-0.101(22)
y44m	0.142(24)
y44p	0.008(16)
PVII peak type	
FWHM = a + b/Cos(Th) + c Tan(Th)	
a	0.000766512
b	0.006068987
c	0.1576263
Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)	
ma	0.06540861
mb	0.005475635

mc	0.004191095
Lattice parameters	
a (Å)	9.7766(13)
b (Å)	12.98138(96)
c (Å)	13.14494(82)
alpha (°)	110.9527(57)
beta (°)	94.4390(88)
gamma (°)	95.9765(95)

Site	Np	x	y	z	Atom	Occ	Beq
Yb1	2	0.15297	0.35566	0.16909	Yb	1	1
S1	2	0.49312	0.64744	0.47155	S	1	1
S2	2	0.53655	0.20377	-0.04743	S	1	1
S3	2	-0.03347	0.24831	-0.23976	S	1	1
O1	2	0.18500	0.53052	0.15550	O	1	2
H1	2	0.26830	0.57840	0.17880	H	1	4
H2	2	0.13250	0.58000	0.18790	H	1	4
O2	2	0.42460	0.66770	0.21630	O	1	2
H3	2	0.44110	0.70010	0.15740	H	1	4
H4	2	0.47310	0.72220	0.28280	H	1	4
N1	2	0.32790	0.46250	0.31450	N	1	2
N2	2	0.34900	0.33170	0.06650	N	1	2
N3	2	0.05590	0.30030	-0.01950	N	1	2
N4	2	0.26530	0.20290	0.20600	N	1	2
N5	2	-0.00330	0.17030	0.12510	N	1	2
N6	2	0.05360	0.36010	0.34091	N	1	2
N7	2	-0.07820	0.42090	0.18890	N	1	2
N8	2	0.57210	0.89700	0.39650	N	1	2
C1	2	0.39780	0.53890	0.38030	C	1	2
C2	2	0.42720	0.28110	0.01840	C	1	2
C3	2	0.01990	0.27890	-0.11080	C	1	2
C4	2	0.40210	0.21930	0.23800	C	1	2
H4A	2	0.45530	0.28750	0.24430	H	1	4
C5	2	0.46900	0.14060	0.26220	C	1	2
H5A	2	0.56610	0.15450	0.28500	H	1	4
C6	2	0.39200	0.04280	0.25260	C	1	2
H6A	2	0.43510	-0.01300	0.26800	H	1	4
C7	2	0.25240	0.02560	0.22050	C	1	2
H7A	2	0.19780	-0.04210	0.21440	H	1	4
C8	2	0.19040	0.10670	0.19700	C	1	2
C9	2	0.04100	0.09200	0.15900	C	1	2
C10	2	-0.05000	0.00130	0.15540	C	1	2
H10A	2	-0.01730	-0.05270	0.18060	H	1	4
C11	2	-0.18680	-0.01130	0.11600	C	1	2
H11A	2	-0.24970	-0.07310	0.11460	H	1	4
C12	2	-0.23190	0.06600	0.07870	C	1	2
H12A	2	-0.32600	0.05830	0.04910	H	1	4
C13	2	-0.13760	0.15570	0.08500	C	1	2
H13A	2	-0.16910	0.21000	0.05980	H	1	4
C14	2	0.12250	0.33220	0.41680	C	1	2
H14A	2	0.21580	0.31960	0.40910	H	1	4
C15	2	0.06570	0.32090	0.50560	C	1	2
H15A	2	0.11840	0.30130	0.55780	H	1	4
C16	2	-0.06930	0.33880	0.51650	C	1	2
H16A	2	-0.11200	0.33050	0.57620	H	1	4
C17	2	-0.14160	0.36860	0.44070	C	1	2
H17A	2	-0.23500	0.38130	0.44760	H	1	4
C18	2	-0.07830	0.38040	0.35360	C	1	2
C19	2	-0.14810	0.41840	0.27260	C	1	2
C20	2	-0.27670	0.45470	0.28410	C	1	2
H20A	2	-0.32440	0.45250	0.34380	H	1	4
C21	2	-0.33500	0.49390	0.20870	C	1	2
H21A	2	-0.42260	0.51920	0.21610	H	1	4
C22	2	-0.26480	0.49570	0.12300	C	1	2
H22A	2	-0.30280	0.52180	0.06960	H	1	4
C23	2	-0.13770	0.45870	0.11620	C	1	2
H23A	2	-0.08930	0.46000	0.05660	H	1	4

C24	2	0.69470	0.87930	0.35870	C	1	2
H24A	2	0.69860	0.81150	0.29980	H	1	4
C25	2	0.81390	0.95340	0.40040	C	1	2
H25A	2	0.89870	0.93760	0.37160	H	1	4
C26	2	0.80810	1.05060	0.48450	C	1	2
H26A	2	0.88890	1.10440	0.51470	H	1	4
C27	2	0.68360	1.07040	0.52560	C	1	2
H27A	2	0.67800	1.13750	0.58470	H	1	4
C28	2	0.56790	0.99150	0.47970	C	1	2

3Er

File 1 : S:\Andr\Paper\SP_Er_Yb_NCS\Pow\3\Er_NCS_phen\Er_NCS_phen_2018_04_04.raw_1

Range Number : 1

R-Values

Rexp : 4.93 Rwp : 7.15 Rp : 5.60 GOF : 1.45
Rexp`: 2.72 Rwp`: 3.94 Rp` : 3.68 DW : 1.04

Quantitative Analysis - Rietveld

Phase 1 : [Er(H2O)(phen)2(NCS)3]•phen•0.5H2O 100.000 %

Background

One on X		8300(1300)
Chebychev polynomial, Coefficient	0	-315(79)
	1	523(82)
	2	-292(43)
	3	159(22)
	4	-81(11)
	5	41.5(60)
	6	-19.9(29)
	7	12.7(17)

Instrument

Primary radius (mm)	280
Secondary radius (mm)	280
Linear PSD 2Th angular range (°)	2.94
FDS angle (°)	0.9
Beam spill, sample length (mm)	30
Intensity corrected	

Corrections

Specimen displacement	0.2022206
LP Factor	0

Miscellaneous

Start X	5
Finish X	50

Structure 1

Phase name	[Er(H2O)(phen)2(NCS)3]•phen•0.5H2O
R-Bragg	2.509
Spacegroup	P-1
Scale	0.00004059(19)
Cell Mass	1818.328
Cell Volume (Å^3)	1860.03(23)
Wt% - Rietveld	100.000
Crystal Linear Absorption Coeff. (1/cm)	61.2126(77)
Crystal Density (g/cm^3)	1.62331(20)
PVII peak type	
FWHM = a + b/Cos(Th) + c Tan(Th)	

a	0.009437339
b	0.01041474
c	0.1893084
Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)	
ma	0
mb	0
mc	0.061891
Lattice parameters	
a (Å)	10.42599(65)
b (Å)	12.67156(94)
c (Å)	15.2792(10)
alpha (°)	96.7453(54)
beta (°)	104.9875(52)
gamma (°)	103.6756(63)

Site	Np	x	y	z	Atom	Occ	Beq
Er1	2	0.44469	0.29189	0.20935	Er	1	1
S1	2	0.86398	0.21953	0.43319	S	1	1
S2	2	0.85230	0.44161	0.08348	S	1	1
S3	2	0.15545	0.04450	0.38580	S	1	1
O1	2	0.40480	0.44630	0.13910	O	1	2
H1	2	0.42490	0.44490	0.08750	H	1	4
H2	2	0.41310	0.51260	0.16250	H	1	4
O21	2	0.49800	0.57930	0.02910	O	0.25	2
H101	2	0.45580	0.60750	-0.01360	H	0.25	4
H102	2	0.53350	0.61620	0.08400	H	0.25	4
O22	2	0.55600	0.56030	0.03540	O	0.25	2
H112	2	0.58670	0.59470	0.09120	H	0.25	4
H110	2	0.49570	0.59440	0.01620	H	0.25	4
N1	2	0.62070	0.23390	0.31410	N	1	2
N2	2	0.62190	0.33400	0.13400	N	1	2
N3	2	0.29310	0.15510	0.27140	N	1	2
N4	2	0.31960	0.39570	0.30590	N	1	2
N5	2	0.59690	0.46440	0.32880	N	1	2
N6	2	0.23110	0.21820	0.06550	N	1	2
N7	2	0.41480	0.09860	0.11920	N	1	2
N8	2	0.61250	0.70150	0.20760	N	1	2
N9	2	0.33720	0.63710	0.19930	N	1	2
C1	2	0.72340	0.22780	0.36160	C	1	2
C2	2	0.71910	0.37880	0.11480	C	1	2
C3	2	0.23600	0.10730	0.31870	C	1	2
C4	2	0.18500	0.36270	0.29640	C	1	2
H4A	2	0.13290	0.29550	0.25550	H	1	4
C5	2	0.11570	0.42210	0.34400	C	1	2
H5A	2	0.01950	0.39490	0.33620	H	1	4
C6	2	0.18930	0.51920	0.40120	C	1	2
H6A	2	0.14450	0.56110	0.43360	H	1	4
C7	2	0.33130	0.55770	0.41250	C	1	2
C8	2	0.41540	0.66040	0.47180	C	1	2
H8A	2	0.37370	0.70520	0.50430	H	1	4
C9	2	0.55080	0.69350	0.48160	C	1	2
H9A	2	0.60350	0.76150	0.52120	H	1	4
C10	2	0.61780	0.63020	0.43460	C	1	2
C11	2	0.76010	0.66140	0.44430	C	1	2
H11A	2	0.81680	0.72790	0.48440	H	1	4
C12	2	0.81610	0.59690	0.39670	C	1	2
H12A	2	0.91190	0.61860	0.40150	H	1	4
C13	2	0.73170	0.49760	0.34000	C	1	2
H13A	2	0.77290	0.45180	0.30810	H	1	4
C14	2	0.53940	0.52900	0.37500	C	1	2
C15	2	0.39300	0.49240	0.36320	C	1	2
C16	2	0.14060	0.27510	0.03930	C	1	2
H16A	2	0.15510	0.34590	0.07480	H	1	4
C17	2	0.02450	0.23640	-0.03810	C	1	2
H17A	2	-0.03800	0.27980	-0.05410	H	1	4
C18	2	0.00290	0.13480	-0.09020	C	1	2
H18A	2	-0.07450	0.10750	-0.14330	H	1	4

C19	2	0.09480	0.07140	-0.06500	C	1	2
C20	2	0.07810	-0.03460	-0.11530	C	1	2
H20A	2	0.00400	-0.06340	-0.17030	H	1	4
C21	2	0.16650	-0.09600	-0.08610	C	1	2
H21A	2	0.15220	-0.16730	-0.12060	H	1	4
C22	2	0.27870	-0.05570	-0.00570	C	1	2
C23	2	0.37210	-0.11570	0.02610	C	1	2
H23A	2	0.35870	-0.18860	-0.00500	H	1	4
C24	2	0.48240	-0.07000	0.10160	C	1	2
H24A	2	0.54590	-0.11060	0.12410	H	1	4
C25	2	0.50070	0.03850	0.14570	C	1	2
H25A	2	0.57920	0.07030	0.19740	H	1	4
C26	2	0.30400	0.05250	0.04470	C	1	2
C27	2	0.20820	0.11650	0.01490	C	1	2
C28	2	0.74620	0.73240	0.21430	C	1	2
H28A	2	0.78260	0.68680	0.17820	H	1	4
C29	2	0.83520	0.82800	0.27150	C	1	2
H29A	2	0.93040	0.84630	0.27440	H	1	4
C30	2	0.78620	0.89580	0.32370	C	1	2
H30A	2	0.84670	0.96180	0.36260	H	1	4
C31	2	0.64620	0.86720	0.31920	C	1	2
C32	2	0.58660	0.93470	0.36840	C	1	2
H32A	2	0.64410	1.00110	0.40840	H	1	4
C33	2	0.44960	0.90720	0.36000	C	1	2
H33A	2	0.41200	0.95490	0.39320	H	1	4
C34	2	0.36090	0.80700	0.30160	C	1	2
C35	2	0.21950	0.77460	0.29280	C	1	2
H35A	2	0.17860	0.82020	0.32510	H	1	4
C36	2	0.14070	0.67670	0.23750	C	1	2
H36A	2	0.04420	0.65390	0.22990	H	1	4
C37	2	0.20400	0.61130	0.19240	C	1	2
H37A	2	0.14770	0.54350	0.15410	H	1	4
C38	2	0.41550	0.73570	0.25250	C	1	2
C39	2	0.56220	0.76680	0.25990	C	1	2

3Yb

File 1 : S:\Andr\Paper\SP_Er_Yb_NCS\Pow\3\Yb_NCS_phen\Yb_NCS_phen_2018_04_04.raw_1

Range Number : 1

R-Values

Rexp : 5.97 Rwp : 8.28 Rp : 6.58 GOF : 1.39
Rexp`: 11.53 Rwp`: 15.98 Rp` : 13.66 DW : 1.08

Number of independent parameters : 17

Quantitative Analysis - Rietveld

Phase 1 : [Yb(H2O)(phen)2(NCS)3]•phen•0.5H2O 100.000 %

Background

Chebychev polynomial, Coefficient	0	146.01(79)
	1	-26.67(85)
	2	4.51(91)
	3	10.14(74)
	4	-6.31(73)

Instrument

Primary radius (mm)	280
Secondary radius (mm)	280
Linear PSD 2Th angular range (°)	2.94
FDS angle (°)	1
Beam spill, sample length (mm)	25

Intensity corrected

Corrections

Specimen displacement	0.3349183
LP Factor	0

Miscellaneous

Start X	5
Finish X	50

Structure 1

Phase name	[Yb(H2O)(phen)2(NCS)3]•phen•0.5H2O
R-Bragg	2.294
Spacegroup	P-1
Scale	0.00002764(19)
Cell Mass	1829.887
Cell Volume (Å^3)	1850.12(32)
Wt% - Rietveld	100.000
Crystal Linear Absorption Coeff. (1/cm)	66.463(11)
Crystal Density (g/cm^3)	1.64238(28)
Preferred Orientation Spherical Harmonics	
Order	2
y00	1
y20	0.009(15)
y21m	0.078(12)
y21p	0.022(12)
y22m	0.004(14)
y22p	0.088(13)
PVII peak type	
FWHM = a + b/Cos(Th) + c Tan(Th)	
a	0.004810939
b	0.005862314
c	0.2590598
Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)	
ma	0
mb	0
mc	0.04134817
Lattice parameters	
a (Å)	10.40415(84)
b (Å)	12.6562(13)
c (Å)	15.2670(14)
alpha (°)	96.8115(73)
beta (°)	105.1554(71)
gamma (°)	103.6804(84)

Site	Np	x	y	z	Atom	Occ	Beq
Yb1	2	0.44470	0.29143	0.20922	Yb	1	1
S1	2	0.86398	0.21953	0.43319	S	1	1
S2	2	0.85230	0.44161	0.08348	S	1	1
S3	2	0.15545	0.04450	0.38580	S	1	1
O1	2	0.40480	0.44630	0.13910	O	1	2
H1	2	0.42490	0.44490	0.08750	H	1	4
H2	2	0.41310	0.51260	0.16250	H	1	4
O21	2	0.49800	0.57930	0.02910	O	0.25	2
H101	2	0.45580	0.60750	-0.01360	H	0.25	4
H102	2	0.53350	0.61620	0.08400	H	0.25	4
O22	2	0.55600	0.56030	0.03540	O	0.25	2
H112	2	0.58670	0.59470	0.09120	H	0.25	4
H110	2	0.49570	0.59440	0.01620	H	0.25	4
N1	2	0.62070	0.23390	0.31410	N	1	2
N2	2	0.62190	0.33400	0.13400	N	1	2
N3	2	0.29310	0.15510	0.27140	N	1	2
N4	2	0.31960	0.39570	0.30590	N	1	2
N5	2	0.59690	0.46440	0.32880	N	1	2
N6	2	0.23110	0.21820	0.06550	N	1	2
N7	2	0.41480	0.09860	0.11920	N	1	2

N8	2	0.61250	0.70150	0.20760	N	1	2
N9	2	0.33720	0.63710	0.19930	N	1	2
C1	2	0.72340	0.22780	0.36160	C	1	2
C2	2	0.71910	0.37880	0.11480	C	1	2
C3	2	0.23600	0.10730	0.31870	C	1	2
C4	2	0.18500	0.36270	0.29640	C	1	2
H4A	2	0.13290	0.29550	0.25550	H	1	4
C5	2	0.11570	0.42210	0.34400	C	1	2
H5A	2	0.01950	0.39490	0.33620	H	1	4
C6	2	0.18930	0.51920	0.40120	C	1	2
H6A	2	0.14450	0.56110	0.43360	H	1	4
C7	2	0.33130	0.55770	0.41250	C	1	2
C8	2	0.41540	0.66040	0.47180	C	1	2
H8A	2	0.37370	0.70520	0.50430	H	1	4
C9	2	0.55080	0.69350	0.48160	C	1	2
H9A	2	0.60350	0.76150	0.52120	H	1	4
C10	2	0.61780	0.63020	0.43460	C	1	2
C11	2	0.76010	0.66140	0.44430	C	1	2
H11A	2	0.81680	0.72790	0.48440	H	1	4
C12	2	0.81610	0.59690	0.39670	C	1	2
H12A	2	0.91190	0.61860	0.40150	H	1	4
C13	2	0.73170	0.49760	0.34000	C	1	2
H13A	2	0.77290	0.45180	0.30810	H	1	4
C14	2	0.53940	0.52900	0.37500	C	1	2
C15	2	0.39300	0.49240	0.36320	C	1	2
C16	2	0.14060	0.27510	0.03930	C	1	2
H16A	2	0.15510	0.34590	0.07480	H	1	4
C17	2	0.02450	0.23640	-0.03810	C	1	2
H17A	2	-0.03800	0.27980	-0.05410	H	1	4
C18	2	0.00290	0.13480	-0.09020	C	1	2
H18A	2	-0.07450	0.10750	-0.14330	H	1	4
C19	2	0.09480	0.07140	-0.06500	C	1	2
C20	2	0.07810	-0.03460	-0.11530	C	1	2
H20A	2	0.00400	-0.06340	-0.17030	H	1	4
C21	2	0.16650	-0.09600	-0.08610	C	1	2
H21A	2	0.15220	-0.16730	-0.12060	H	1	4
C22	2	0.27870	-0.05570	-0.00570	C	1	2
C23	2	0.37210	-0.11570	0.02610	C	1	2
H23A	2	0.35870	-0.18860	-0.00500	H	1	4
C24	2	0.48240	-0.07000	0.10160	C	1	2
H24A	2	0.54590	-0.11060	0.12410	H	1	4
C25	2	0.50070	0.03850	0.14570	C	1	2
H25A	2	0.57920	0.07030	0.19740	H	1	4
C26	2	0.30400	0.05250	0.04470	C	1	2
C27	2	0.20820	0.11650	0.01490	C	1	2
C28	2	0.74620	0.73240	0.21430	C	1	2
H28A	2	0.78260	0.68680	0.17820	H	1	4
C29	2	0.83520	0.82800	0.27150	C	1	2
H29A	2	0.93040	0.84630	0.27440	H	1	4
C30	2	0.78620	0.89580	0.32370	C	1	2
H30A	2	0.84670	0.96180	0.36260	H	1	4
C31	2	0.64620	0.86720	0.31920	C	1	2
C32	2	0.58660	0.93470	0.36840	C	1	2
H32A	2	0.64410	1.00110	0.40840	H	1	4
C33	2	0.44960	0.90720	0.36000	C	1	2
H33A	2	0.41200	0.95490	0.39320	H	1	4
C34	2	0.36090	0.80700	0.30160	C	1	2
C35	2	0.21950	0.77460	0.29280	C	1	2
H35A	2	0.17860	0.82020	0.32510	H	1	4
C36	2	0.14070	0.67670	0.23750	C	1	2
H36A	2	0.04420	0.65390	0.22990	H	1	4
C37	2	0.20400	0.61130	0.19240	C	1	2
H37A	2	0.14770	0.54350	0.15410	H	1	4
C38	2	0.41550	0.73570	0.25250	C	1	2
C39	2	0.56220	0.76680	0.25990	C	1	2

4Er

File 1 : G:\Andr\Paper\SP_Er_Yb_NCS\Pow\4\Er_NCS_bpy_HNCS\Er_NCS_bpy_HNCS_2018_04_25.raw_1

Range Number : 1

R-Values

Rexp : 4.37	Rwp : 8.09	Rp : 5.75	GOF : 1.85
Rexp`: 8.93	Rwp`: 16.51	Rp` : 13.39	DW : 1.17

Number of independent parameters : 14

Quantitative Analysis - Rietveld

Phase 1 : [Hbpy][Er(NCS)4(bpy)2]	100.000 %

Background

One on X		0(510)
Chebychev polynomial, Coefficient	0	295(32)
	1	-15(33)
	2	-10(17)
	3	-14.8(88)
	4	8.8(42)
	5	-8.6(25)

Instrument

Primary radius (mm)	280
Secondary radius (mm)	280
Linear PSD 2Th angular range (°)	2.94
FDS angle (°)	1.2
Beam spill, sample length (mm)	18
Intensity corrected	

Corrections

Specimen displacement	0.2324584
LP Factor	0

Miscellaneous

Start X	5
Finish X	50

hkl Phase - 1 Lebail method

Phase name		[Hbpy][Er(NCS)4(bpy)2]
R-Bragg		0.957
Spacegroup		P-1
Cell Mass		1738.31
Cell Volume (Å^3)		1795.66(13)
Wt% - Rietveld		100.000
Crystallite Size		
Cry size Lorentzian (nm)		190.8(28)
PV_MOD peak type: a + b Tan(Th) + c / Cos(Th)		
FWHM a		0.0001000024
b		0.0746289
c		0.0001000024
Lorentzian mix a		0.0001000024
b		0.212323
c		0.0001000024
Lattice parameters		
a (Å)		9.65697(39)
b (Å)		13.28613(38)
c (Å)		16.30576(63)
alpha (°)		112.3937(28)
beta (°)		94.5259(37)
gamma (°)		107.8103(32)

4Yb

File 1 : G:\Andr\Paper\SP_Er_Yb_NCS\Pow\4\Yb_NCS_bpy_HNCS\Yb_NCS_bpy_HNCS_2018_04_25.raw_1

Range Number : 1

R-Values

Rexp : 2.98	Rwp : 8.59	Rp : 5.86	GOF : 2.88
Rexp`: 6.39	Rwp`: 18.44	Rp` : 14.53	DW : 1.15

Quantitative Analysis - Rietveld

Phase 1 : [Hbpy][Yb(NCS)4(bpy)2]	100.000 %

Background

Chebychev polynomial, Coefficient	0	675.4(22)
	1	167.0(37)
	2	6.2(34)
	3	-39.4(33)
	4	28.4(30)
	5	-21.8(30)

Instrument

Primary radius (mm)	280
Secondary radius (mm)	280
Linear PSD 2Th angular range (°)	2.94
FDS angle (°)	1.2
Beam spill, sample length (mm)	18
Intensity corrected	

Corrections

Specimen displacement	-0.0009435189
LP Factor	0

Miscellaneous

Start X	5
Finish X	50

hkl Phase - 1 Lebail method

Phase name		[Hbpy][Yb(NCS)4(bpy)2]
R-Bragg		0.994
Spacegroup		P-1
Cell Mass		1749.870
Cell Volume (Å^3)		1788.68(15)
Wt% - Rietveld		100.000
PV_MOD peak type: a + b Tan(Th) + c / Cos(Th)		
FWHM a		0.04983109
b		0.0001
c		0.01439521
Lorentzian mix a		0.8456502
b		0.0001
c		0.3323685
Lattice parameters		
a (Å)		9.64083(51)
b (Å)		13.27715(39)
c (Å)		16.29354(72)
alpha (°)		112.4800(28)
beta (°)		94.4975(43)
gamma (°)		107.8313(36)

5Er

File 1 : S:\Andr\Paper\SP_Er_Yb_NCS\Pow\5\Er_NCS_phen_HNCS\Er_NCS_phen_HNCS_2018_05_04.raw_1

Range Number : 1

R-Values

Rexp : 2.92	Rwp : 7.26	Rp : 5.64	GOF : 2.48
Rexp`: 3.27	Rwp`: 8.12	Rp` : 7.05	DW : 0.39

Number of independent parameters : 17

Quantitative Analysis - Rietveld

Phase 1 : [Hphen][Er(NCS)4(phen)2]	100.000 %

Background

One on X		9200(1900)
Chebychev polynomial, Coefficient	0	70(140)
	1	660(150)
	2	-469(84)
	3	207(47)
	4	-94(26)
	5	45(15)
	6	-31.8(75)
	7	55.1(48)

Instrument

Primary radius (mm)	280
Secondary radius (mm)	280
Linear PSD 2Th angular range (°)	2.94
FDS angle (°)	1
Beam spill, sample length (mm)	25
Intensity corrected	

Corrections

Specimen displacement	0.2
LP Factor	0

Miscellaneous

Start X	4
Finish X	50

Structure 1

Phase name		[Hphen][Er(NCS)4(phen)2]
R-Bragg		3.933
Spacegroup		P21/n
Scale		0.00002210(12)
Cell Mass		3764.933
Cell Volume (Å^3)		3873.24(35)
Wt% - Rietveld		100.000
Crystal Linear Absorption Coeff. (1/cm)		63.7363(58)
Crystal Density (g/cm^3)		1.61411(15)
Preferred Orientation (Dir 1 : 1 -1 -1)		0.5756(51)
(Dir 2 : 0 1 0)		0.674(12)
Fraction of Dir 1		0.693(19)
PV_MOD peak type: a + b Tan(Th) + c / Cos(Th)		
FWHM a		0.04(43)
b		0.083(80)
c		0.04(43)
Lorentzian mix a		0.5(50)
b		0.24(99)
c		0.1(50)
Lattice parameters		
a (Å)		12.44936(54)

b (Å)		16.59200(74)
c (Å)		18.7695(12)
beta (°)		92.5343(42)

Site	Np	x	y	z	Atom	Occ	Beq
Er1	4	0.54633	0.18304	0.28683	Er	1	1
S1	4	0.93692	0.14932	0.21442	S	1	1
S2	4	0.16074	0.19907	0.36177	S	1	1
S3	4	0.66095	-0.05586	0.45204	S	1	1
S4	4	0.43193	-0.03896	0.10436	S	1	1
N1	4	0.72213	0.14473	0.25352	N	1	2
N2	4	0.36687	0.15324	0.32178	N	1	2
N3	4	0.58815	0.07378	0.36676	N	1	2
N4	4	0.49369	0.07428	0.20809	N	1	2
N5	4	0.54746	0.24790	0.40855	N	1	2
N6	4	0.67062	0.30797	0.30471	N	1	2
N7	4	0.43707	0.31657	0.26737	N	1	2
N8	4	0.55056	0.24397	0.16469	N	1	2
N9	4	0.69372	0.08338	0.57529	N	1	2
H1	4	0.71500	0.05630	0.53630	H	1	4
N10	4	0.81207	0.15041	0.47210	N	1	2
C1	4	0.81170	0.14556	0.23681	C	1	2
C2	4	0.28060	0.17089	0.33912	C	1	2
C3	4	0.61911	0.02041	0.40218	C	1	2
C4	4	0.46783	0.02686	0.16507	C	1	2
C5	4	0.49200	0.21745	0.46062	C	1	2
H5A	4	0.46320	0.16400	0.45530	H	1	4
C6	4	0.47350	0.25985	0.52307	C	1	2
H6A	4	0.43290	0.23560	0.55910	H	1	4
C7	4	0.51450	0.33656	0.53152	C	1	2
H7A	4	0.50140	0.36680	0.57310	H	1	4
C8	4	0.57610	0.37050	0.47873	C	1	2
C9	4	0.62600	0.44941	0.48467	C	1	2
H9A	4	0.61540	0.48160	0.52560	H	1	4
C10	4	0.68730	0.47858	0.43365	C	1	2
H10A	4	0.71920	0.53100	0.43910	H	1	4
C11	4	0.70560	0.43257	0.37152	C	1	2
C12	4	0.77180	0.45955	0.31798	C	1	2
H12A	4	0.80560	0.51150	0.32160	H	1	4
C13	4	0.78770	0.41156	0.26104	C	1	2
H13A	4	0.83310	0.42920	0.22480	H	1	4
C14	4	0.73608	0.33578	0.25647	C	1	2
H14A	4	0.74860	0.30240	0.21660	H	1	4
C15	4	0.65672	0.35501	0.36266	C	1	2
C16	4	0.59155	0.32392	0.41737	C	1	2
C17	4	0.37659	0.35153	0.31476	C	1	2
H17A	4	0.35680	0.32010	0.35440	H	1	4
C18	4	0.33990	0.43229	0.30994	C	1	2
H18A	4	0.29520	0.45430	0.34490	H	1	4
C19	4	0.36960	0.47861	0.25420	C	1	2
H19A	4	0.34770	0.53400	0.25080	H	1	4
C20	4	0.43230	0.44452	0.20205	C	1	2
C21	4	0.46680	0.48919	0.14191	C	1	2
H21A	4	0.44860	0.54520	0.13730	H	1	4
C22	4	0.52410	0.45367	0.09242	C	1	2
H22A	4	0.54690	0.48510	0.05370	H	1	4
C23	4	0.55220	0.36865	0.09632	C	1	2
C24	4	0.60660	0.32845	0.04379	C	1	2
H24A	4	0.62720	0.35710	0.00290	H	1	4
C25	4	0.63020	0.24769	0.05122	C	1	2
H25A	4	0.66520	0.21900	0.01500	H	1	4
C26	4	0.60190	0.20789	0.11337	C	1	2
H26A	4	0.62050	0.15210	0.11890	H	1	4
C27	4	0.52280	0.32368	0.15595	C	1	2
C28	4	0.46294	0.36177	0.20975	C	1	2
C29	4	0.63590	0.04593	0.62260	C	1	2
H29A	4	0.61410	-0.00900	0.61510	H	1	4

C30	4	0.60710	0.08643	0.68276	C	1	2
H30A	4	0.56490	0.05970	0.71660	H	1	4
C31	4	0.63970	0.16546	0.69362	C	1	2
H31A	4	0.62050	0.19340	0.73520	H	1	4
C32	4	0.70140	0.20510	0.64337	C	1	2
C33	4	0.73730	0.28746	0.64971	C	1	2
H33A	4	0.72140	0.31770	0.69080	H	1	4
C34	4	0.79300	0.32298	0.59898	C	1	2
H34A	4	0.81460	0.37820	0.60450	H	1	4
C35	4	0.82065	0.27956	0.53646	C	1	2
C36	4	0.87770	0.31401	0.48118	C	1	2
H36A	4	0.90120	0.36910	0.48390	H	1	4
C37	4	0.89900	0.26788	0.42397	C	1	2
H37A	4	0.93650	0.29060	0.38590	H	1	4
C38	4	0.86490	0.18613	0.42146	C	1	2
H38A	4	0.88080	0.15480	0.38100	H	1	4
C39	4	0.78929	0.19759	0.52839	C	1	2
C40	4	0.72858	0.16164	0.58301	C	1	2

5Yb

File 1 : S:\Andr\Paper\SP_Er_Yb_NCS\Pow\5\Yb_NCS_phen_HNCS\Yb_NCS_phen_HNCS_2018_05_04.raw_1

Range Number : 1

R-Values

Rexp : 3.96 Rwp : 8.06 Rp : 6.28 GOF : 2.04
Rexp`: 8.72 Rwp`: 17.76 Rp` : 16.17 DW : 0.71

Number of independent parameters : 14

Quantitative Analysis - Rietveld

Phase 1 : [Hphen][Yb(NCS)4(phen)2] 100.000 %

Background

Chebychev polynomial, Coefficient	0	385.0(14)
	1	-44.9(20)
	2	-19.0(19)
	3	-9.1(18)
	4	6.6(16)
	5	-17.1(16)

Instrument

Primary radius (mm)	280
Secondary radius (mm)	280
Linear PSD 2Th angular range (°)	2.94
FDS angle (°)	1
Beam spill, sample length (mm)	30
Intensity corrected	

Corrections

Specimen displacement	0.2767687
LP Factor	0

Miscellaneous

Start X	4
Finish X	50

Structure 1

Phase name	[Hphen][Yb(NCS)4(phen)2]
R-Bragg	3.174
Spacegroup	P21/n

Scale	0.000010700(60)
Cell Mass	3788.049
Cell Volume (Å^3)	3862.45(32)
Wt% - Rietveld	100.000
Crystal Linear Absorption Coeff. (1/cm)	68.6296(56)
Crystal Density (g/cm^3)	1.62855(13)
Preferred Orientation (Dir 1 : 1 -1 -1)	0.7433(64)
(Dir 2 : 0 1 0)	0.672(39)
Fraction of Dir 1	0.853(32)
PVII peak type	
FWHM = a + b/Cos(Th) + c Tan(Th)	
a	0.009147276
b	0.02198601
c	0.005215139
Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)	
ma	0.1347203
mb	0.009668545
mc	0.04065351
Lattice parameters	
a (Å)	12.44280(49)
b (Å)	16.59188(76)
c (Å)	18.7246(10)
beta (°)	92.3426(38)

Site	Np	x	y	z	Atom	Occ	Beq
Yb1	4	0.55090	0.17621	0.28812	Yb	1	1
S1	4	0.93692	0.14932	0.21442	S	1	1
S2	4	0.16074	0.19907	0.36177	S	1	1
S3	4	0.66095	-0.05586	0.45204	S	1	1
S4	4	0.43193	-0.03896	0.10436	S	1	1
N1	4	0.72213	0.14473	0.25352	N	1	2
N2	4	0.36687	0.15324	0.32178	N	1	2
N3	4	0.58815	0.07378	0.36676	N	1	2
N4	4	0.49369	0.07428	0.20809	N	1	2
N5	4	0.54746	0.24790	0.40855	N	1	2
N6	4	0.67062	0.30797	0.30471	N	1	2
N7	4	0.43707	0.31657	0.26737	N	1	2
N8	4	0.55056	0.24397	0.16469	N	1	2
N9	4	0.69372	0.08338	0.57529	N	1	2
H1	4	0.71500	0.05630	0.53630	H	1	4
N10	4	0.81207	0.15041	0.47210	N	1	2
C1	4	0.81170	0.14556	0.23681	C	1	2
C2	4	0.28060	0.17089	0.33912	C	1	2
C3	4	0.61911	0.02041	0.40218	C	1	2
C4	4	0.46783	0.02686	0.16507	C	1	2
C5	4	0.49200	0.21745	0.46062	C	1	2
H5A	4	0.46320	0.16400	0.45530	H	1	4
C6	4	0.47350	0.25985	0.52307	C	1	2
H6A	4	0.43290	0.23560	0.55910	H	1	4
C7	4	0.51450	0.33656	0.53152	C	1	2
H7A	4	0.50140	0.36680	0.57310	H	1	4
C8	4	0.57610	0.37050	0.47873	C	1	2
C9	4	0.62600	0.44941	0.48467	C	1	2
H9A	4	0.61540	0.48160	0.52560	H	1	4
C10	4	0.68730	0.47858	0.43365	C	1	2
H10A	4	0.71920	0.53100	0.43910	H	1	4
C11	4	0.70560	0.43257	0.37152	C	1	2
C12	4	0.77180	0.45955	0.31798	C	1	2
H12A	4	0.80560	0.51150	0.32160	H	1	4
C13	4	0.78770	0.41156	0.26104	C	1	2
H13A	4	0.83310	0.42920	0.22480	H	1	4
C14	4	0.73608	0.33578	0.25647	C	1	2
H14A	4	0.74860	0.30240	0.21660	H	1	4
C15	4	0.65672	0.35501	0.36266	C	1	2
C16	4	0.59155	0.32392	0.41737	C	1	2
C17	4	0.37659	0.35153	0.31476	C	1	2
H17A	4	0.35680	0.32010	0.35440	H	1	4

C18	4	0.33990	0.43229	0.30994	C	1	2
H18A	4	0.29520	0.45430	0.34490	H	1	4
C19	4	0.36960	0.47861	0.25420	C	1	2
H19A	4	0.34770	0.53400	0.25080	H	1	4
C20	4	0.43230	0.44452	0.20205	C	1	2
C21	4	0.46680	0.48919	0.14191	C	1	2
H21A	4	0.44860	0.54520	0.13730	H	1	4
C22	4	0.52410	0.45367	0.09242	C	1	2
H22A	4	0.54690	0.48510	0.05370	H	1	4
C23	4	0.55220	0.36865	0.09632	C	1	2
C24	4	0.60660	0.32845	0.04379	C	1	2
H24A	4	0.62720	0.35710	0.00290	H	1	4
C25	4	0.63020	0.24769	0.05122	C	1	2
H25A	4	0.66520	0.21900	0.01500	H	1	4
C26	4	0.60190	0.20789	0.11337	C	1	2
H26A	4	0.62050	0.15210	0.11890	H	1	4
C27	4	0.52280	0.32368	0.15595	C	1	2
C28	4	0.46294	0.36177	0.20975	C	1	2
C29	4	0.63590	0.04593	0.62260	C	1	2
H29A	4	0.61410	-0.00900	0.61510	H	1	4
C30	4	0.60710	0.08643	0.68276	C	1	2
H30A	4	0.56490	0.05970	0.71660	H	1	4
C31	4	0.63970	0.16546	0.69362	C	1	2
H31A	4	0.62050	0.19340	0.73520	H	1	4
C32	4	0.70140	0.20510	0.64337	C	1	2
C33	4	0.73730	0.28746	0.64971	C	1	2
H33A	4	0.72140	0.31770	0.69080	H	1	4
C34	4	0.79300	0.32298	0.59898	C	1	2
H34A	4	0.81460	0.37820	0.60450	H	1	4
C35	4	0.82065	0.27956	0.53646	C	1	2
C36	4	0.87770	0.31401	0.48118	C	1	2
H36A	4	0.90120	0.36910	0.48390	H	1	4
C37	4	0.89900	0.26788	0.42397	C	1	2
H37A	4	0.93650	0.29060	0.38590	H	1	4
C38	4	0.86490	0.18613	0.42146	C	1	2
H38A	4	0.88080	0.15480	0.38100	H	1	4
C39	4	0.78929	0.19759	0.52839	C	1	2
C40	4	0.72858	0.16164	0.58301	C	1	2

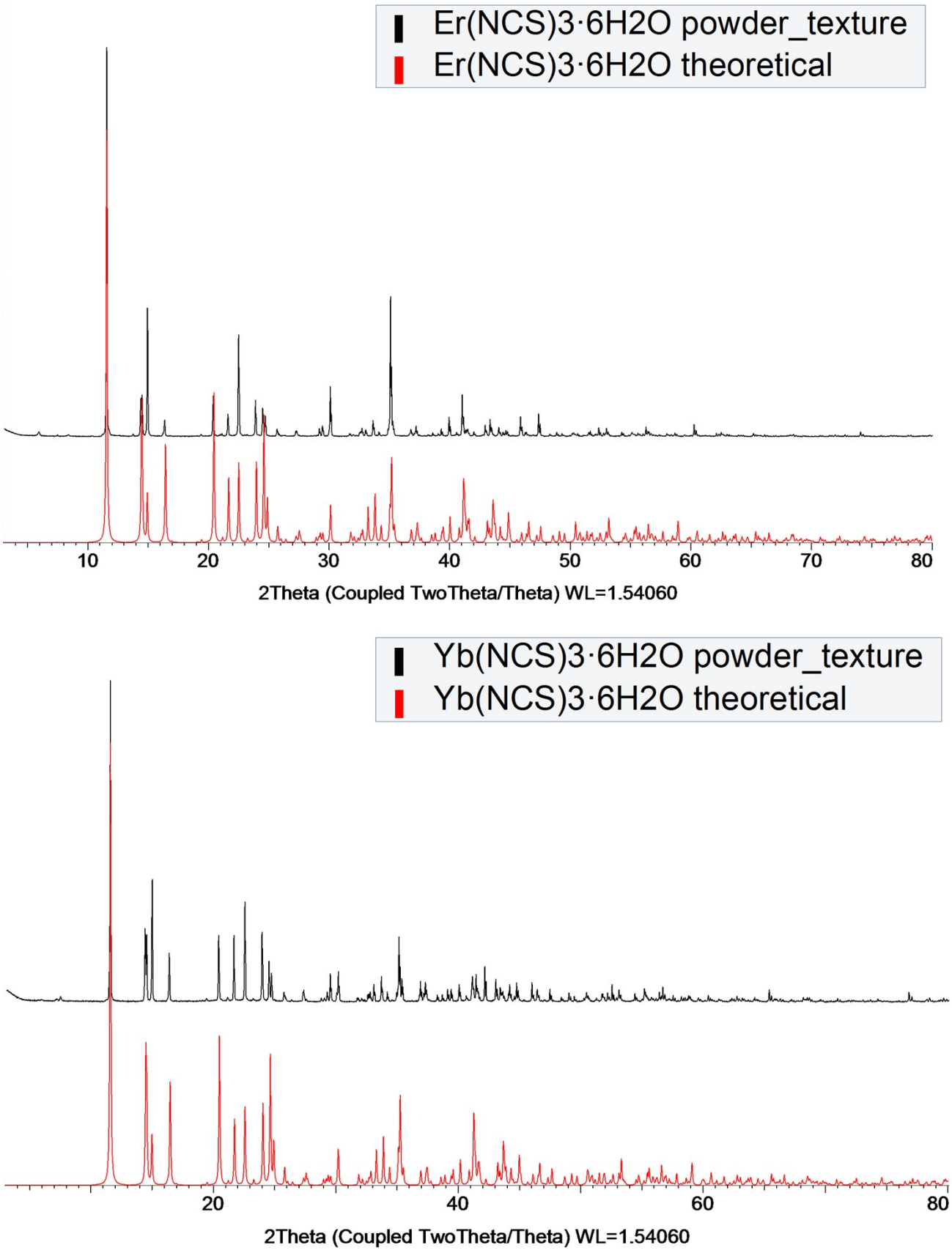
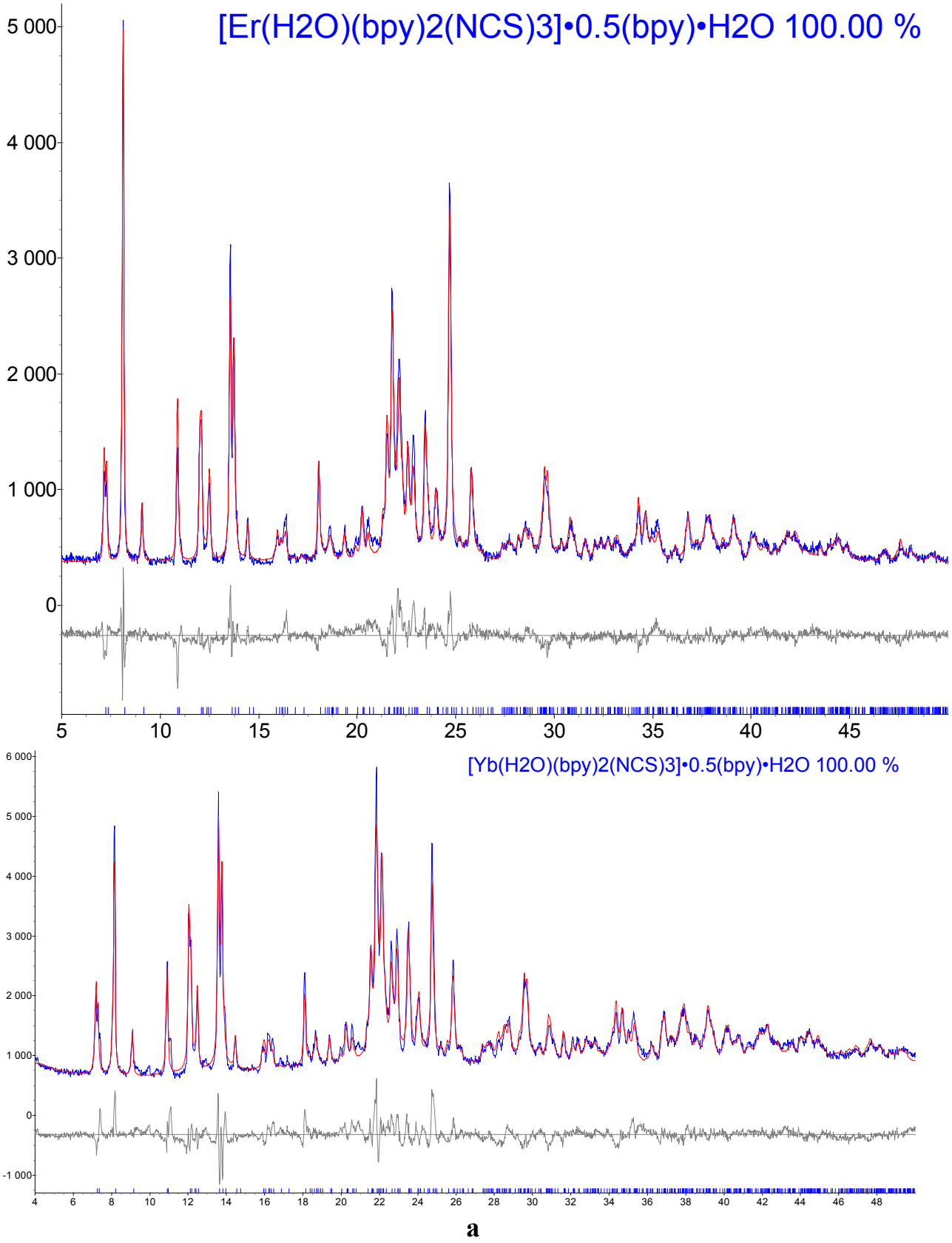


Fig. S1. Experimental and theoretical (considering the texturing) powder XRD patterns of **1Er** and **1Yb**.


[Er(H2O)(bpy)2(NCS)3]•0.5(bpy)•H2O 100.00 %
5 000
4 000
3 000
2 000
1 000
0
5
10
15
20
25
30
35
40
45
[Yb(H2O)(bpy)2(NCS)3]•0.5(bpy)•H2O 100.00 %
6 000
5 000
4 000
3 000
2 000
1 000
0
-1 000
4
6
8
10
12
14
16
18
20
22
24
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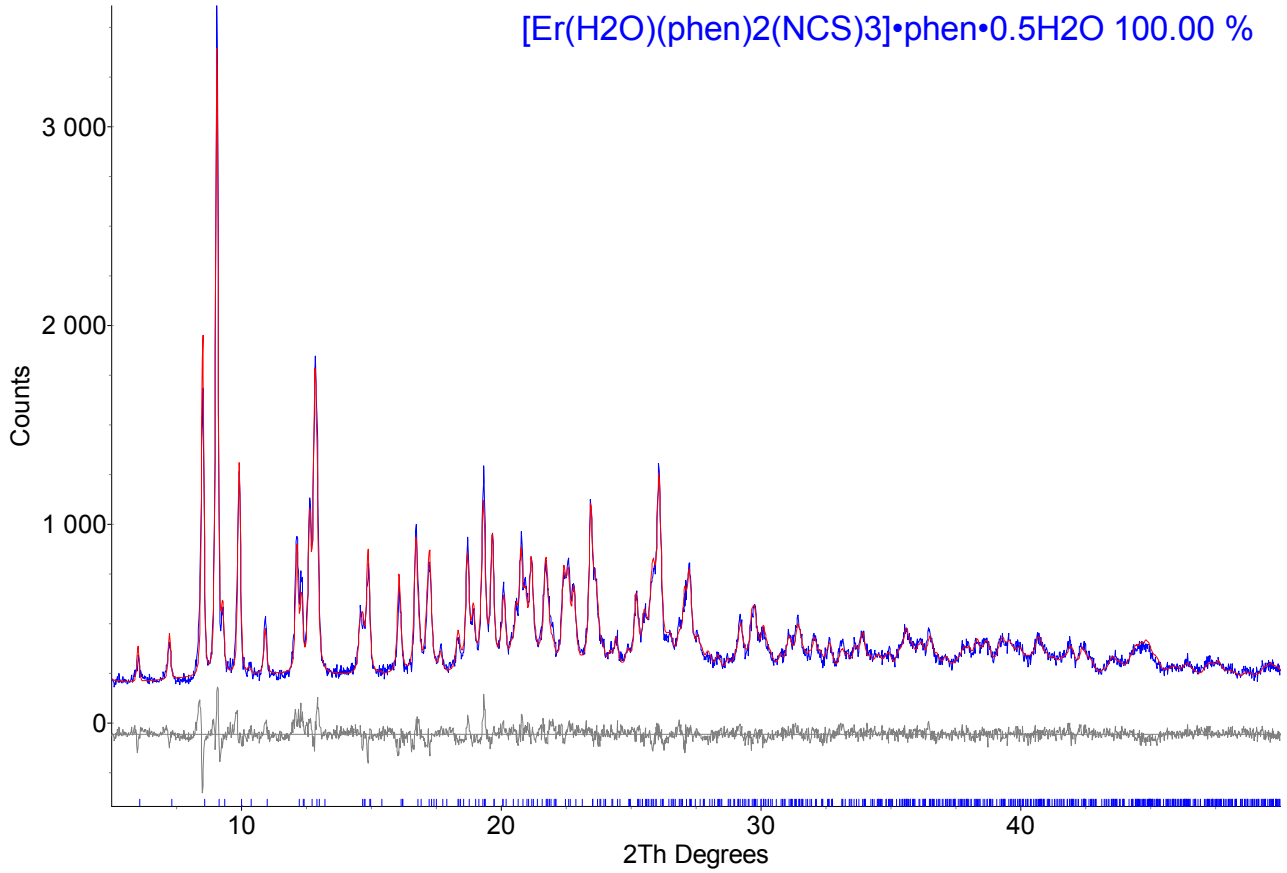
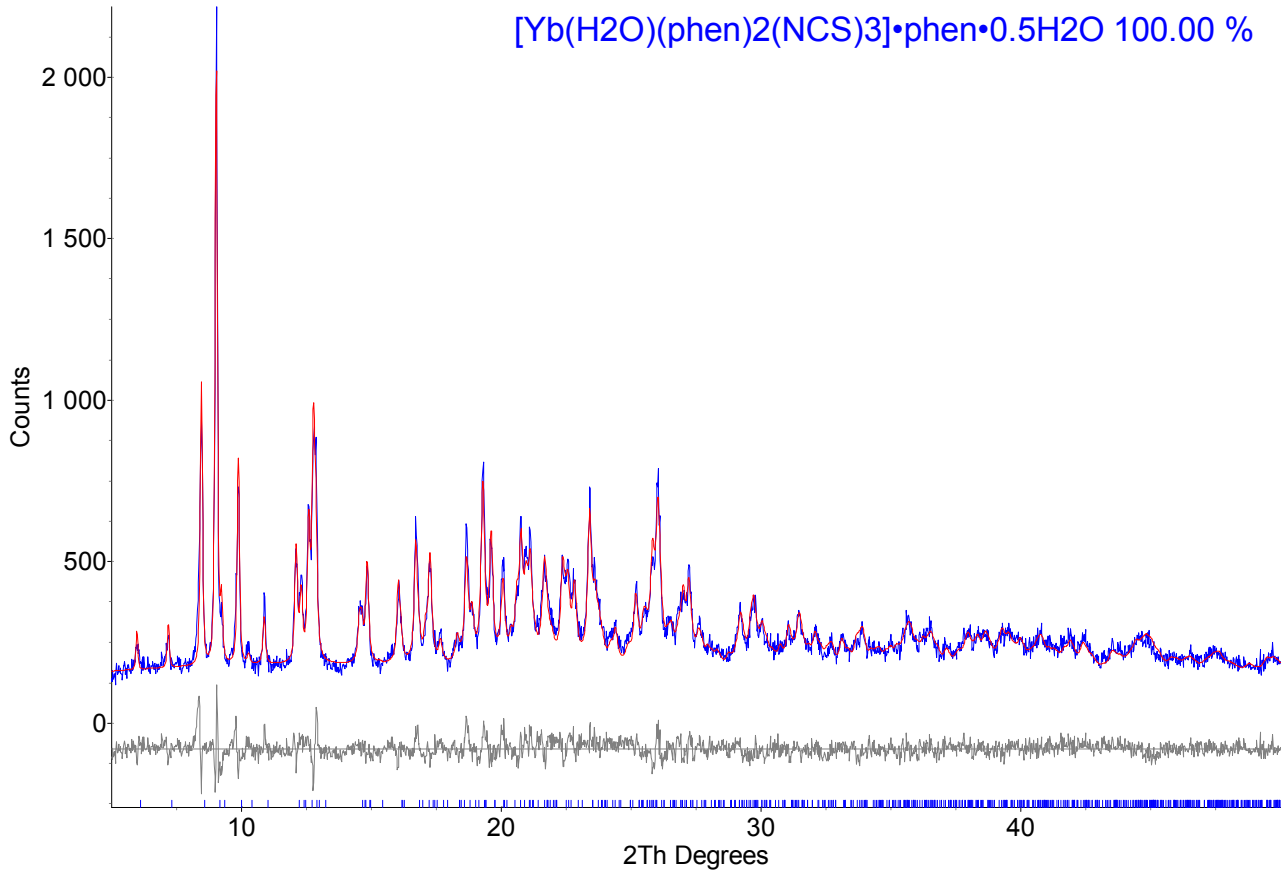
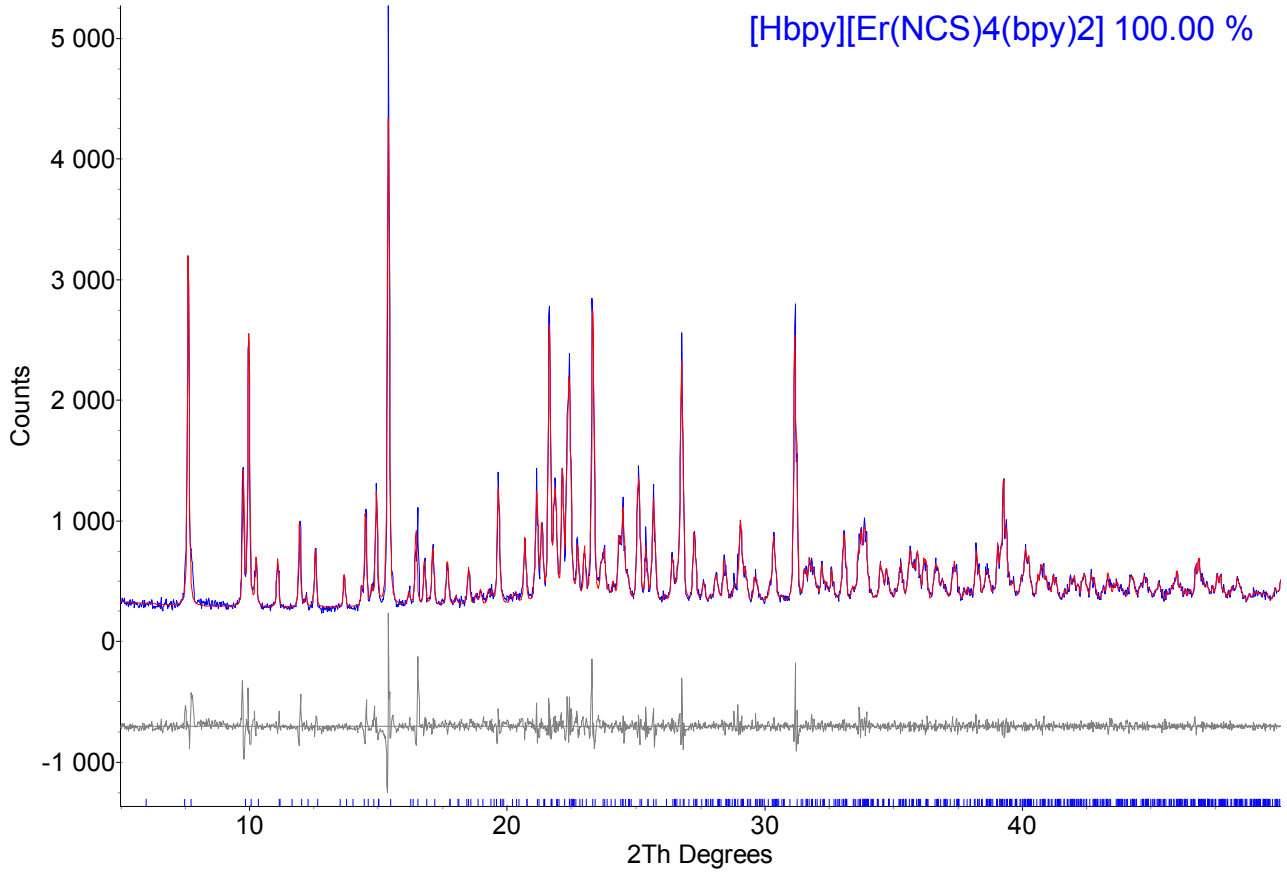
28
30
32
34
36
38
40
42
44
46
48

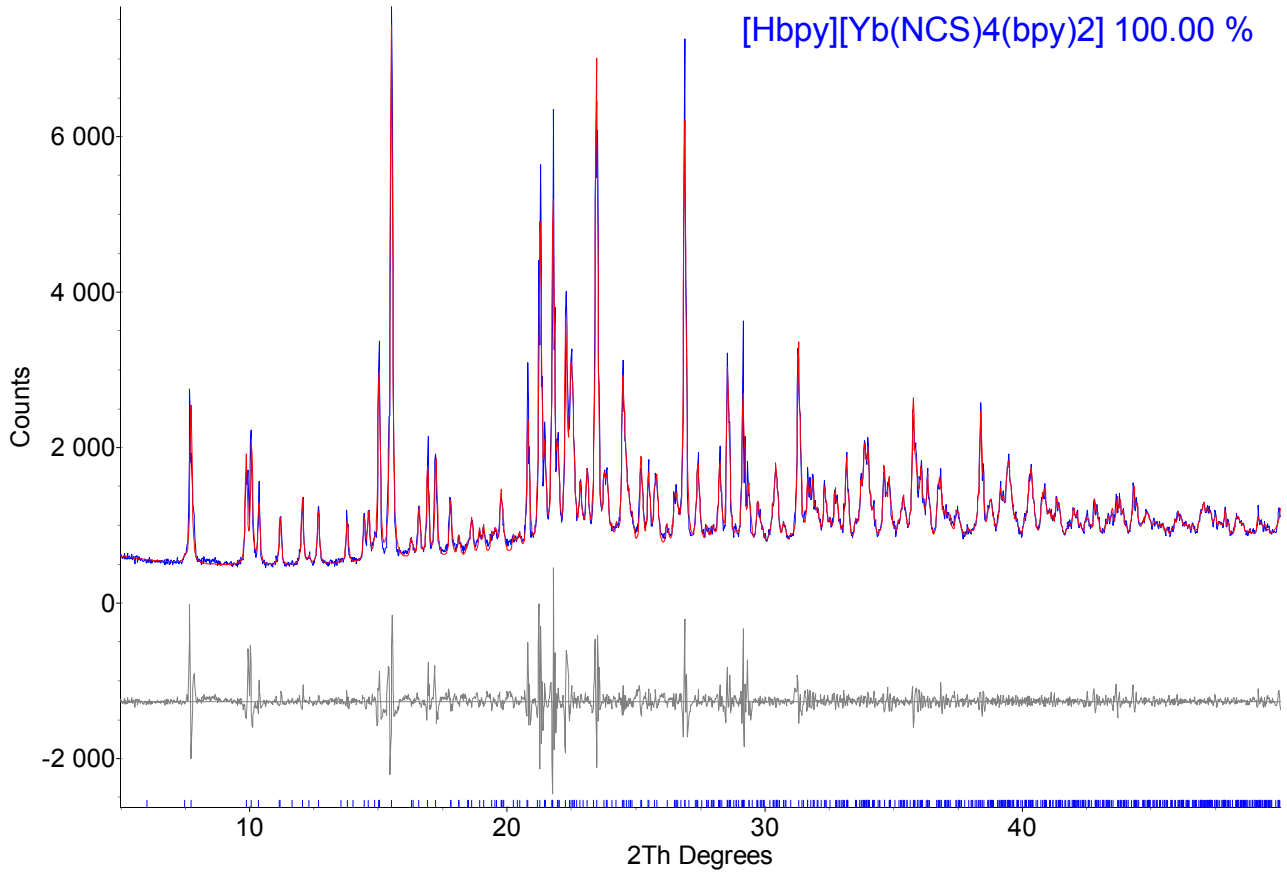
a


[Er(H2O)(phen)2(NCS)3]•phen•0.5H2O 100.00 %
3 000
2 000
1 000
0
Counts
10
20
30
40
2Th Degrees


[Yb(H2O)(phen)2(NCS)3]•phen•0.5H2O 100.00 %
2 000
1 500
1 000
500
0
Counts
10
20
30
40
2Th Degrees

b


[Hbpy][Er(NCS)4(bpy)2] 100.00 %
5 000
4 000
3 000
2 000
1 000
0
-1 000
Counts
10
20
30
40
2Th Degrees


[Hbpy][Yb(NCS)4(bpy)2] 100.00 %
6 000
4 000
2 000
0
-2 000
Counts
10
20
30
40
2Th Degrees

c

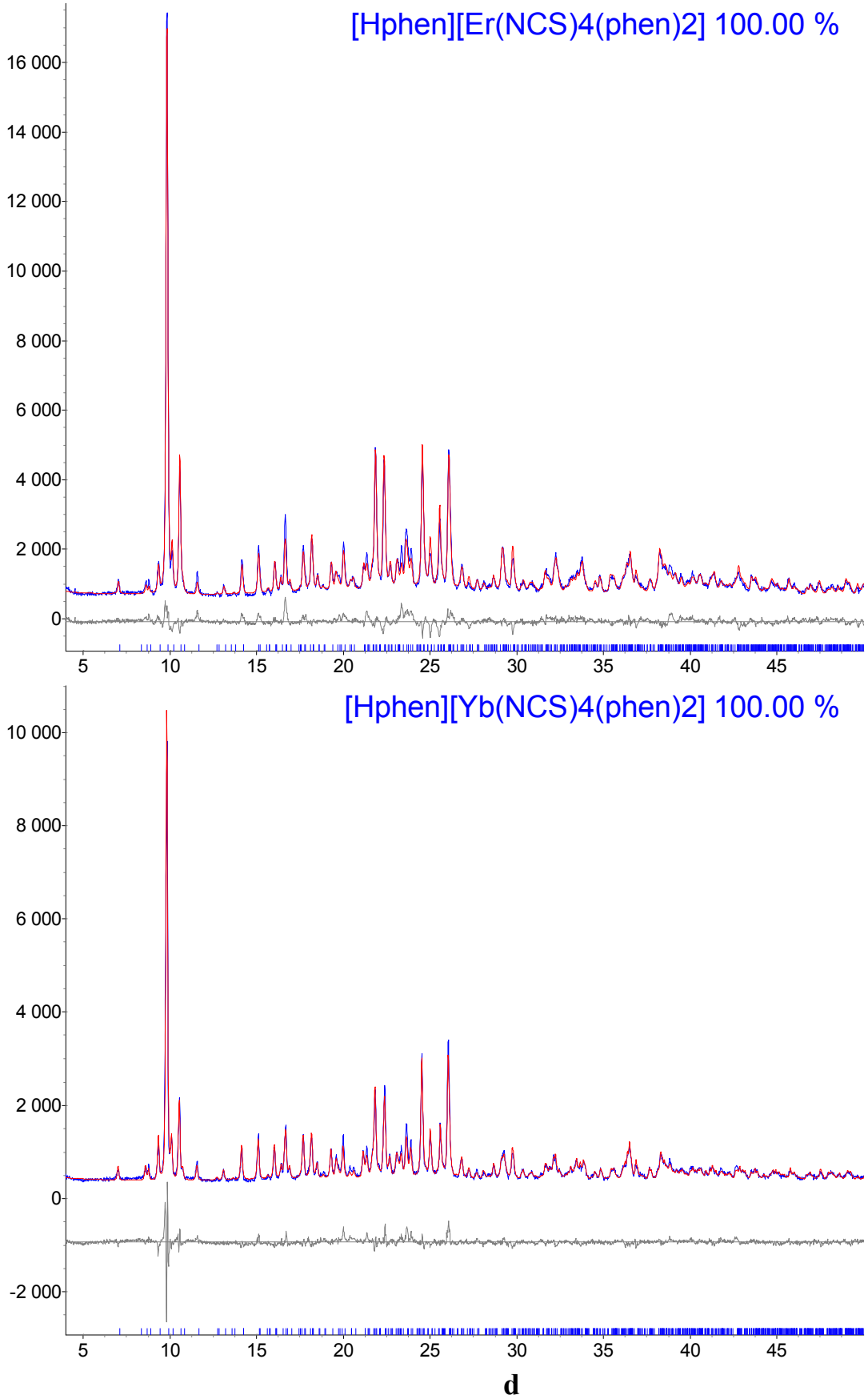


Fig. S2. Rietveld refinement profiles for **2Er**, **2Yb** (**a**); **3Er**, **3Yb** (**b**); **4Er**, **4Yb** (**c**); **5Er**, **5Yb** (**d**) for room temperature powder X-ray data. The calculated and experimental profiles are shown with the red and blue line, respectively. The bottom trace shows the difference curve. The vertical bars indicate the calculated positions of the Bragg peaks.

Thermal behavior of molecular complexes with bpy and phen

According to the results of thermoanalytical studies (Fig. S+3, S+4 Table S2), all the samples lose the outer-sphere H_2O before 75ºC. In the case of **2Er** and **2Yb**, the loss of coordinated H_2O and subsequent elimination of outer-sphere bpy occur in the ranges of 75 – 120 °C and 140-190°C, respectively (Fig.S3, Table S2). For the complexes with 1,10-phenanthroline, coordinated H2O is being lost in 120-160 °C range (Fig.S4, Table S2).

Since all the afore mentioned processes take place at relatively low temperatures, they may also partially occur during the storage of the samples at ambient conditions thus contributing in the discrepancy between calculated and experimental content of the elements.

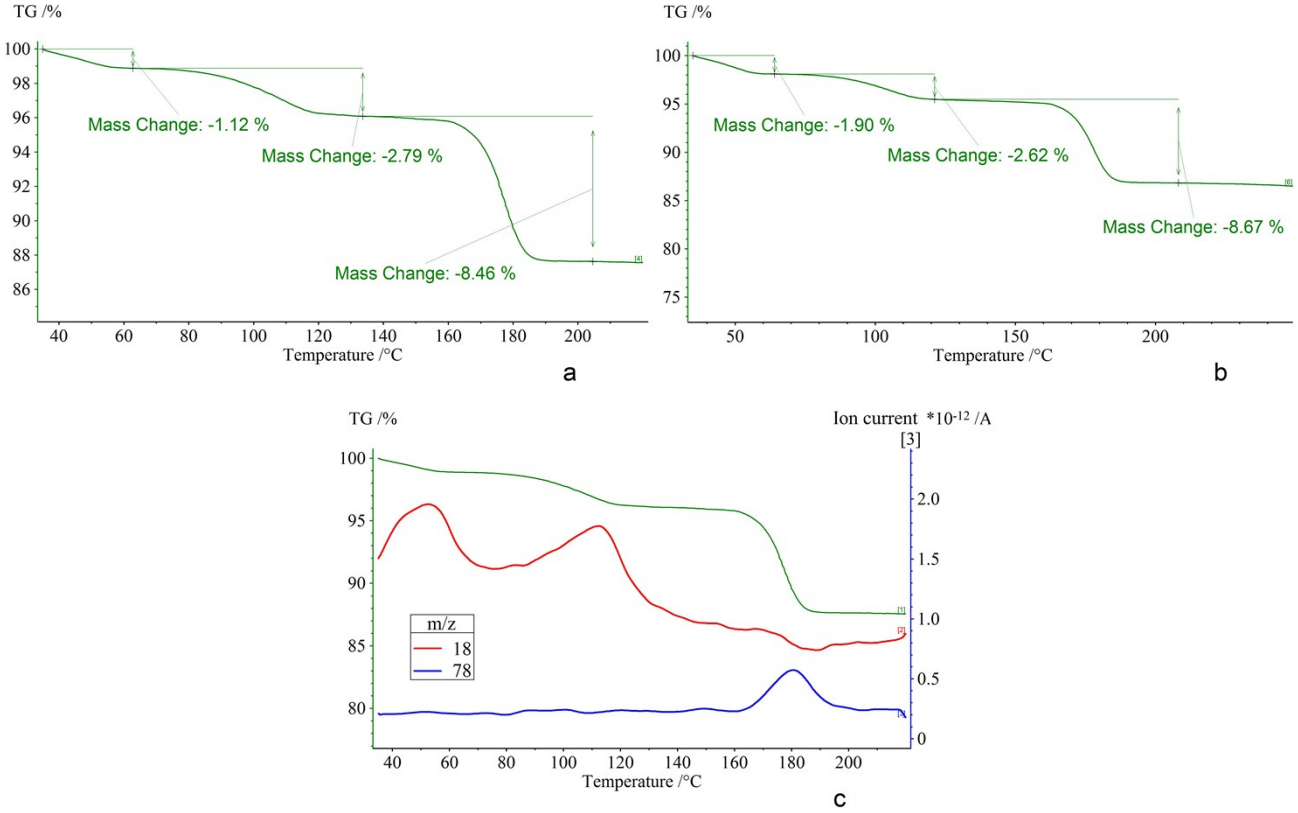


Fig. S3. TG curves of complexes **2Er** (a) and **2Yb** (b) and mass-spectra of gaseous products of decomposition of **2Er** (c) on heating under an Ar flow.

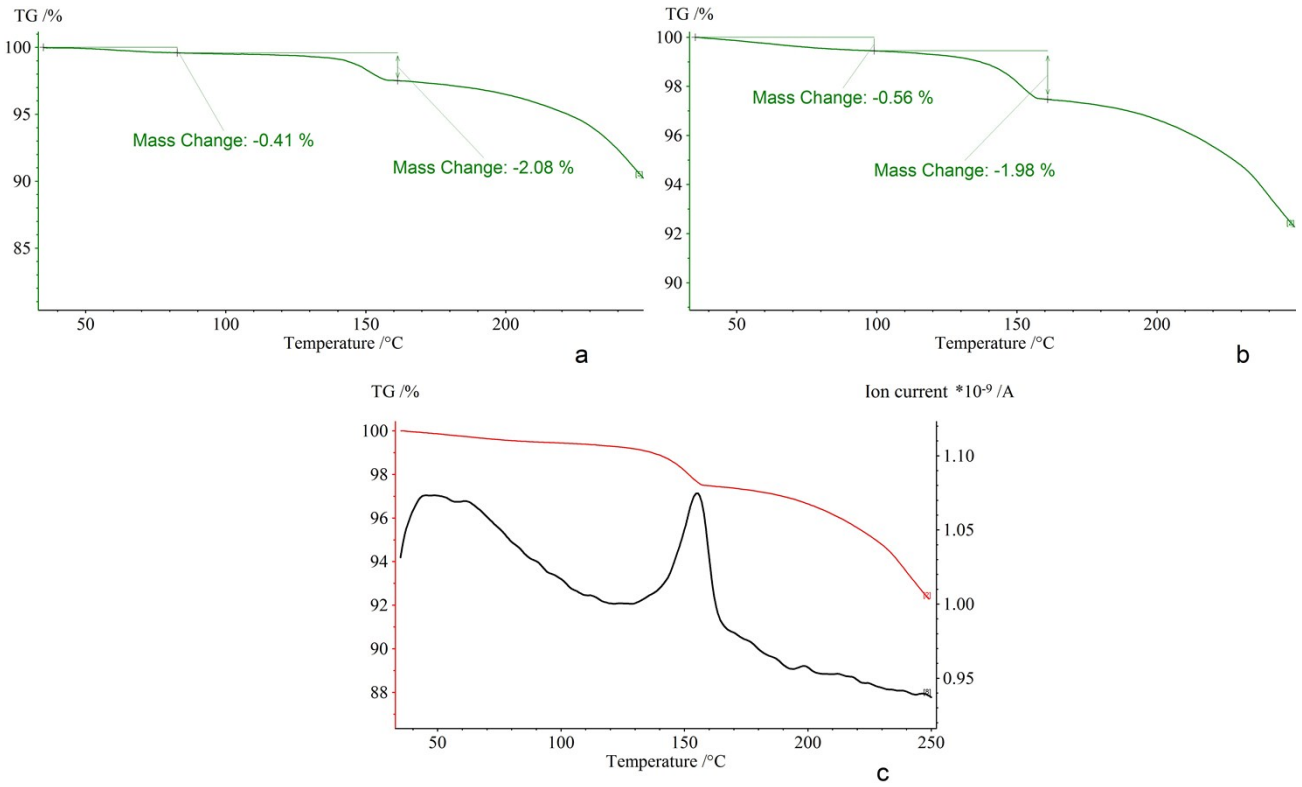


Fig. S4. TG curves of complexes **2Er** (a) and **2Yb** (b) and mass-spectra of gaseous products of decomposition of **2Er** (c) on heating under an Ar flow.

Table S2. Mass loss in a TGA experiment during the elimination of H_2O and outer-sphere molecules.

Complex	**Calculated overall H_2O content, wt. %**	**Mass loss in a TGA experiment, wt. %***		
		Coordinated H_2O	**Outer-sphere H_2O**	**Outer-sphere bpy**
2Er	4.69	-1.12	-2.77	-8.47
2Yb	4.65	-0.63	-2.78	-6.75
3Er	2.97	-0.41	-2.08	-
3Yb	2.95	-0.56	-1.98	-

*Uncertainty of a measurement due to weighting does not exceed 0.2 wt.%; scatter due to uneven solvate molecules evaporation during the storage is higher and can be estimated from $[Yb(H_2O)(bpy)_2(NCS)_3]\cdot 0.5bpy\cdot H_2O$ samples.

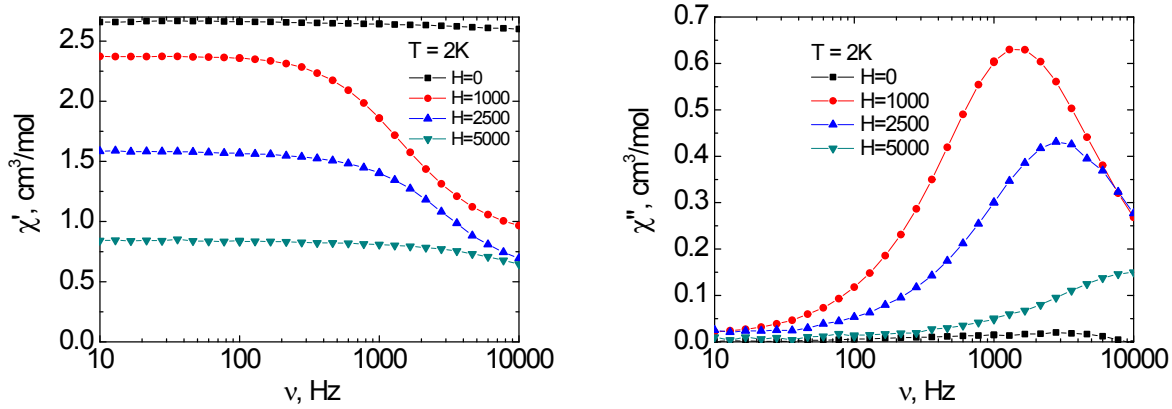


Fig. S5. Frequency dependences of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility at 2 K for **1Er** in various dc-fields.

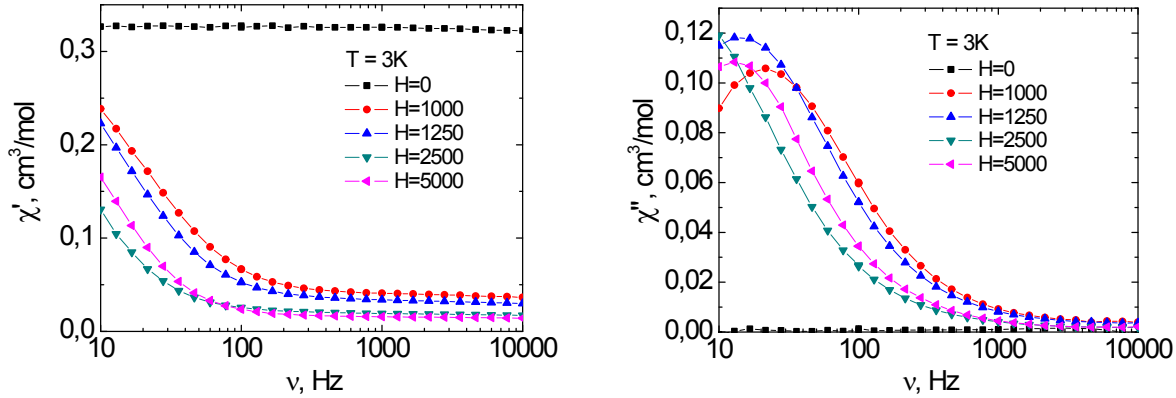


Fig. S6. Frequency dependences of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility at 3 K for **1Yb** in various dc-fields.

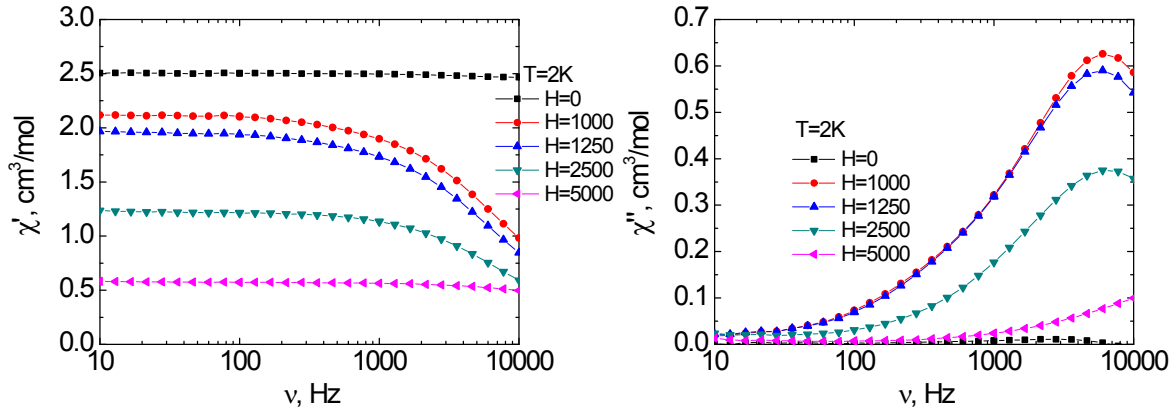


Fig. S7. Frequency dependences of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility at 2 K for **2Er** in various dc-fields.

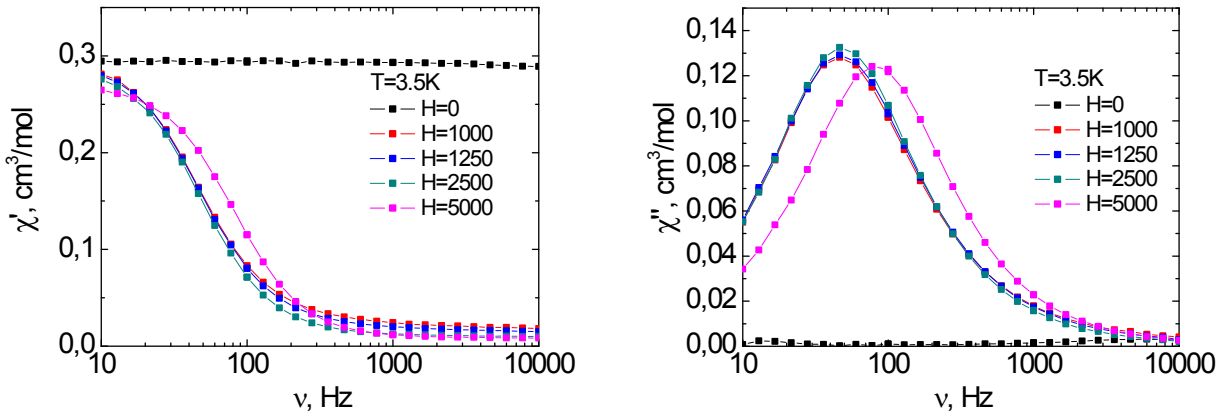


Fig. S8. Frequency dependences of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility at 3.5 K for **2Yb** in various dc-fields.

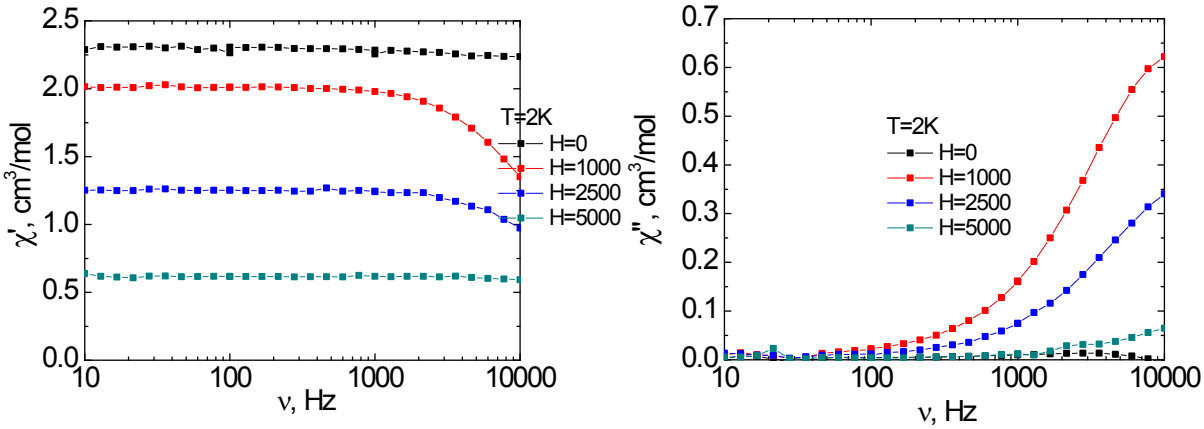


Fig. S9. Frequency dependences of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility at 2 K for **3Er** in various dc-fields.

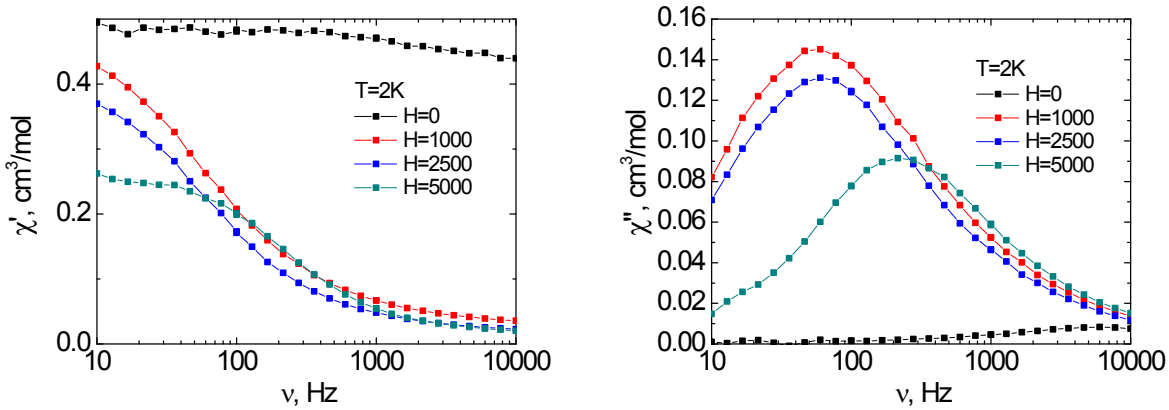


Fig. S10. Frequency dependences of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility at 2 K for **3Yb** in various dc-fields.

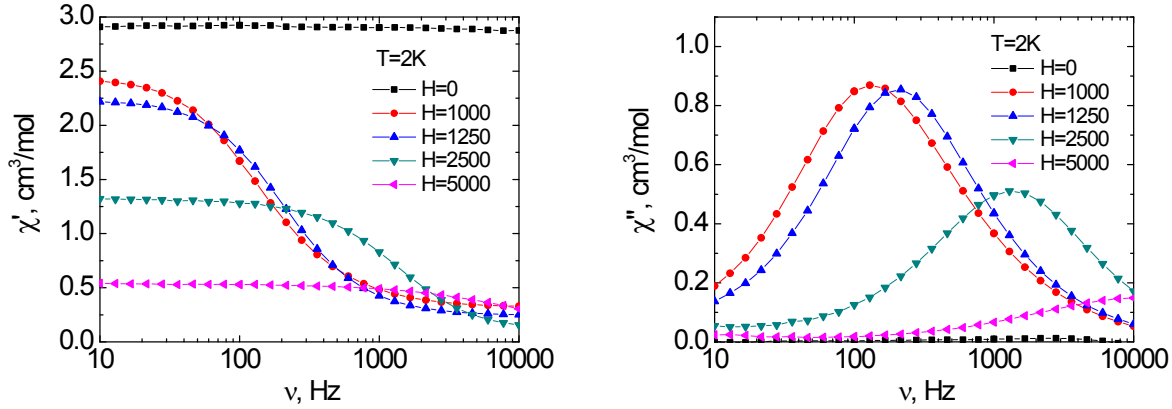


Fig. S11. Frequency dependences of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility at 2 K for **4Er** in various dc-fields.

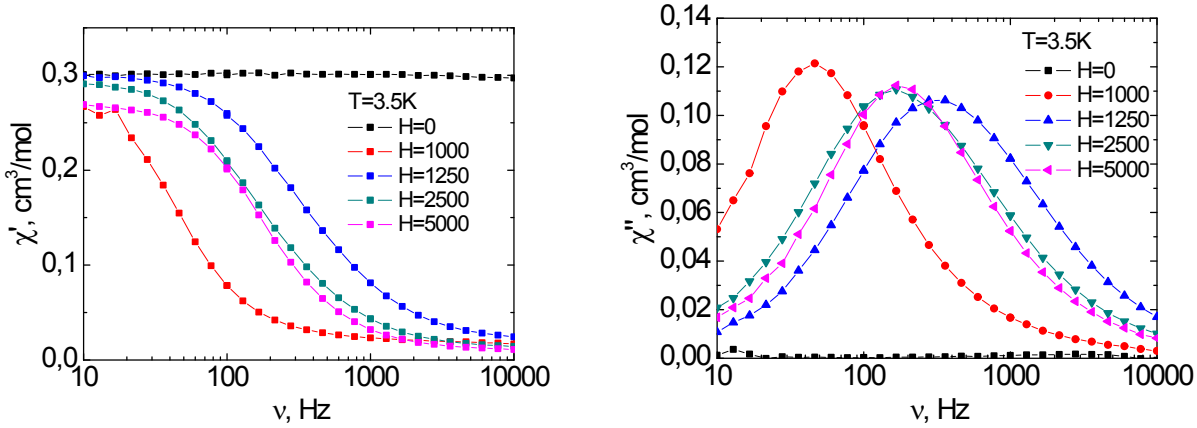


Fig. S12. Frequency dependences of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility at 3.5 K for **4Yb** in various dc-fields.

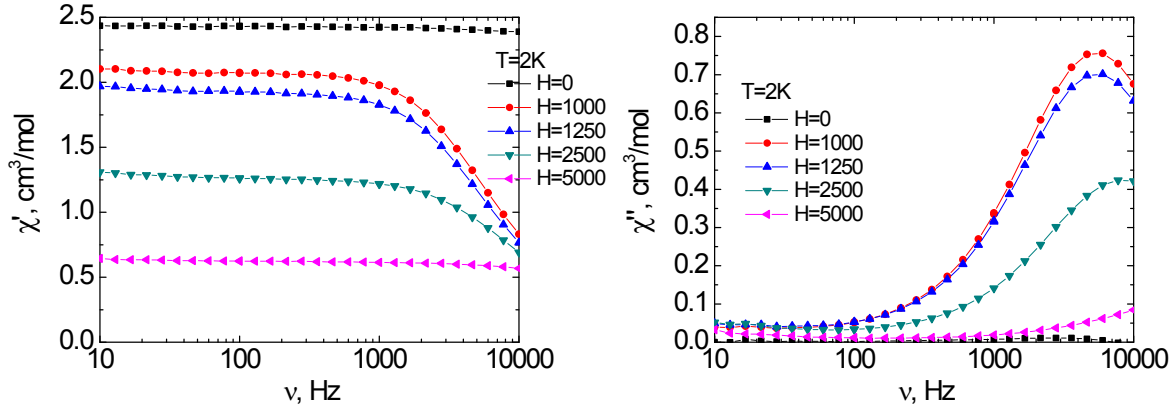


Fig. S13. Frequency dependences of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility at 2 K for **5Er** in various dc-fields.

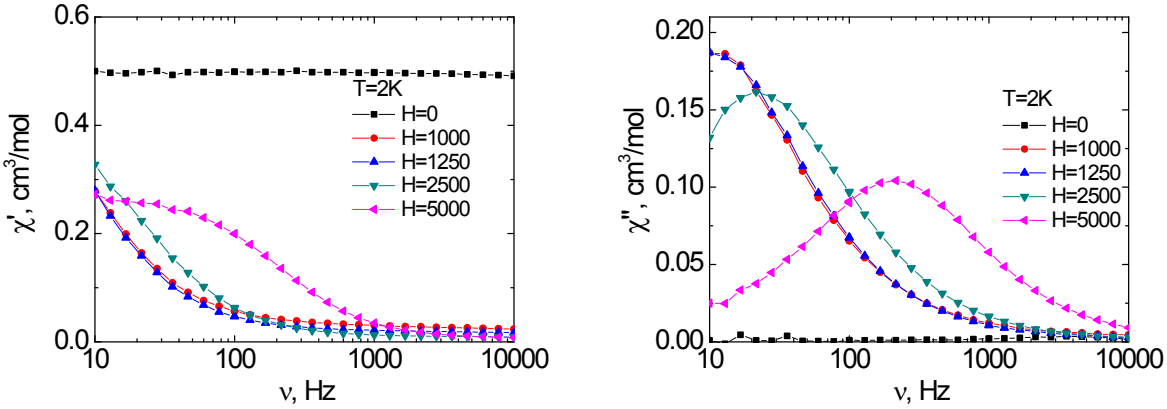


Fig. S14. Frequency dependences of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility at 2 K for **5Yb** in various dc-fields.

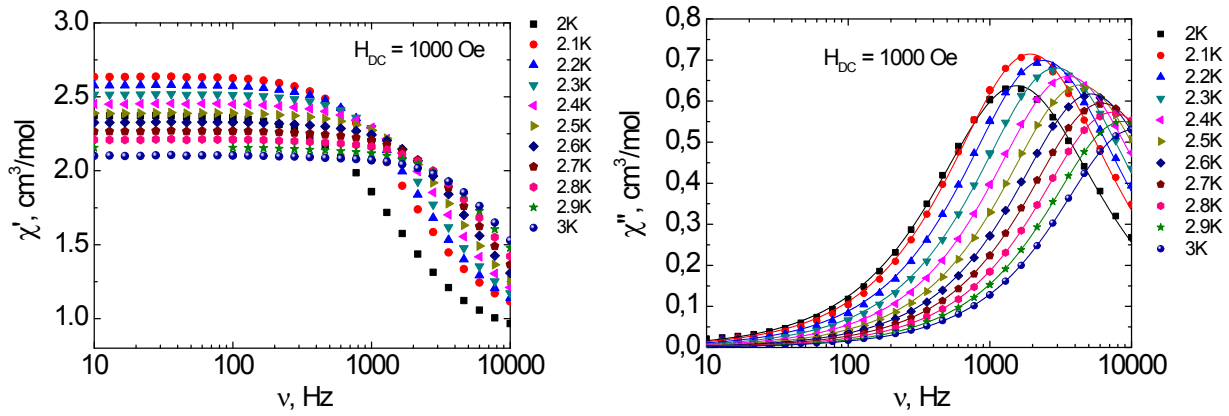


Fig. S15. Frequency dependence of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility between 2 and 3 K for **1Er** in 1000 Oe *dc*-field. Solid lines were fitted using the generalized Debye model.

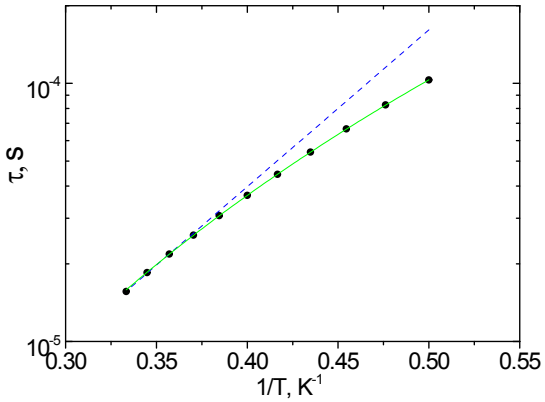


Fig. S16. τ vs. T^{-1} plot for **1Er** in 1000 Oe *dc*-field. Blue dashed line represents the best fit by the Arrhenius equation (Orbach mechanism). Green solid line represents the best fit by the Raman mechanism.

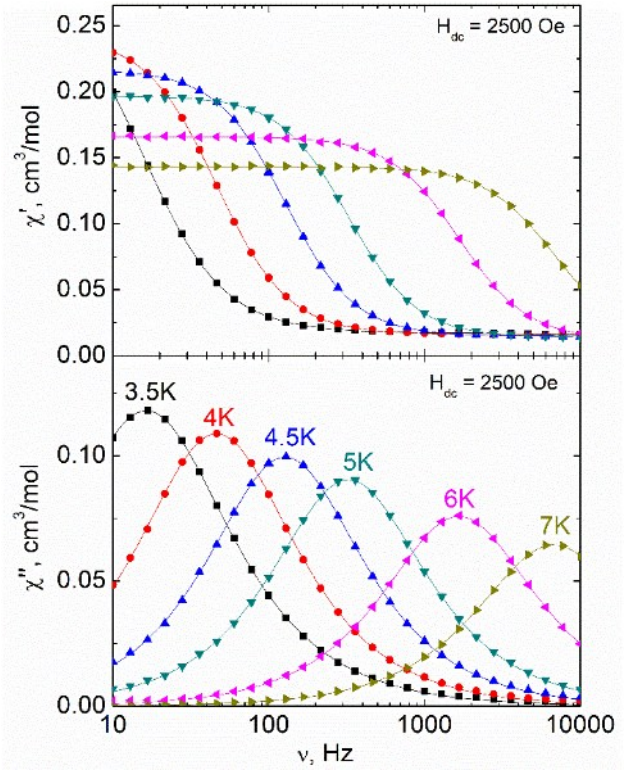


Fig. S17. Frequency dependencies of the real (χ', top) and imaginary (χ'', bottom) components of the *ac* susceptibility between 3.5 and 7 K for **1Yb** in 2500 Oe *dc*-field. Solid lines were fitted using the generalized Debye model.

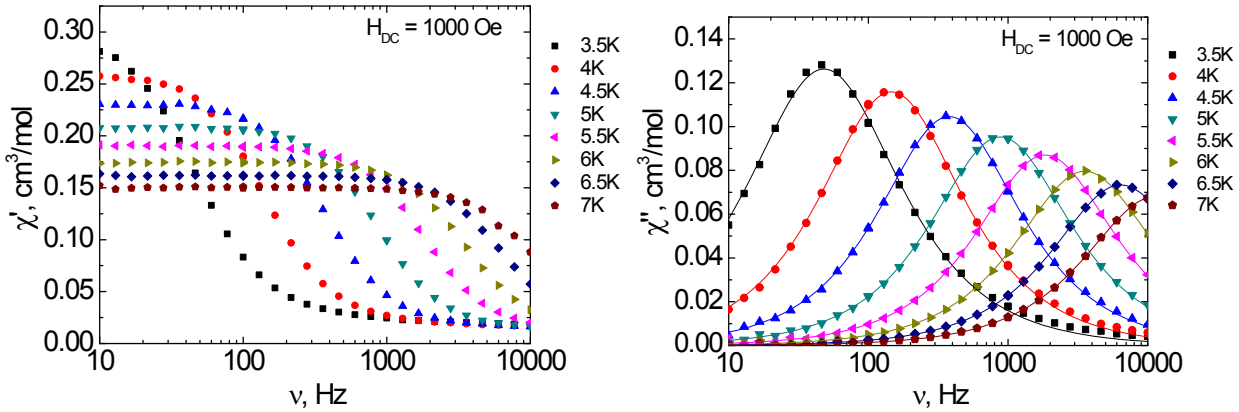


Fig. S18. Frequency dependence of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility between 3.5 and 7 K for **2Yb** in 1000 Oe *dc*-field. Solid lines were fitted using the generalized Debye model.

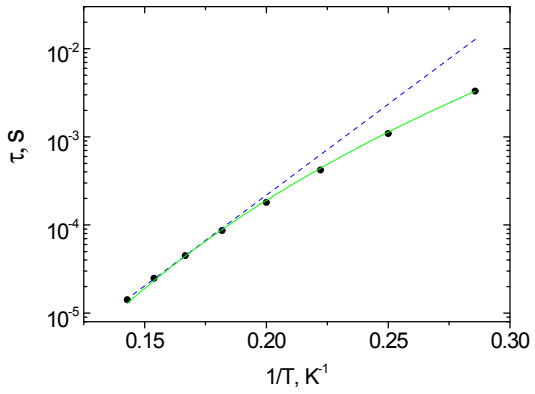


Fig. S19. τ vs. T^{-1} plot for **2Yb** in 1000 Oe *dc*-field. Blue dashed line represents the best fit by the Arrhenius equation (Orbach mechanism). Green solid line represents the best fit by the Raman mechanism.

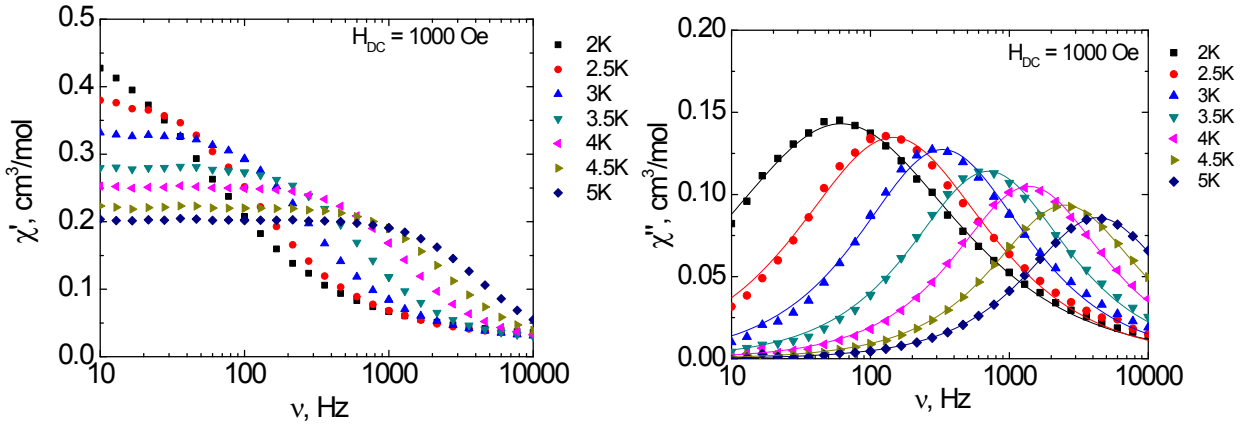


Fig. S20. Frequency dependence of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility between 2 and 5 K for **3Yb** in 1000 Oe *dc*-field. Solid lines were fitted using the generalized Debye model.

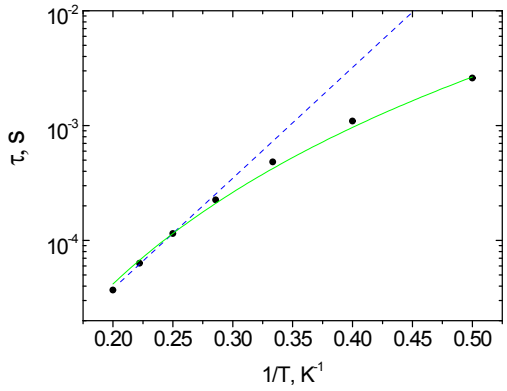


Fig. S21. τ vs. T^{-1} plot for **3Yb** in 1000 Oe *dc*-field. Blue dashed line represents the best fit by the Arrhenius equation (Orbach mechanism). Green solid line represents the best fit by the Raman mechanism.

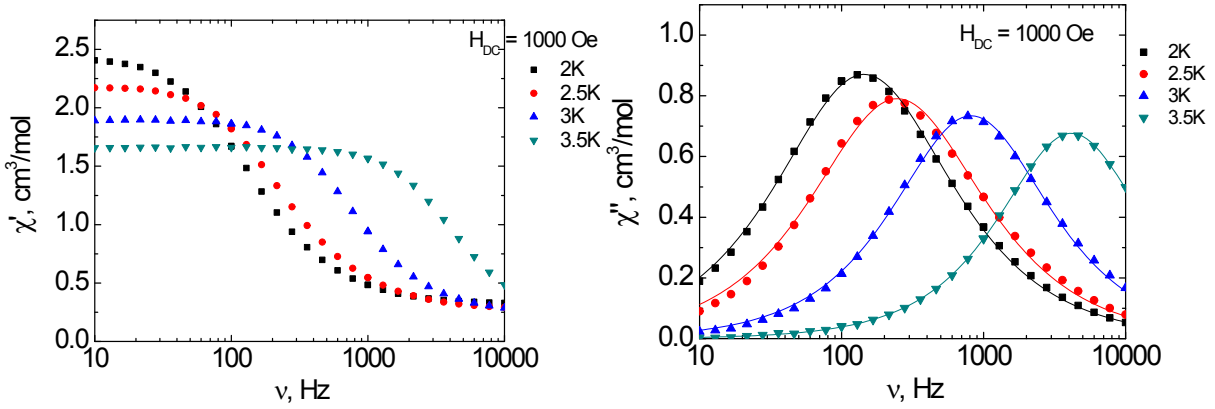


Fig. S22. Frequency dependence of the real (χ', left) and imaginary (χ'', right) components of the ac susceptibility between 2 and 3.5 K for **4Er** in 1000 Oe *dc*-field. Solid lines were fitted using the generalized Debye model.

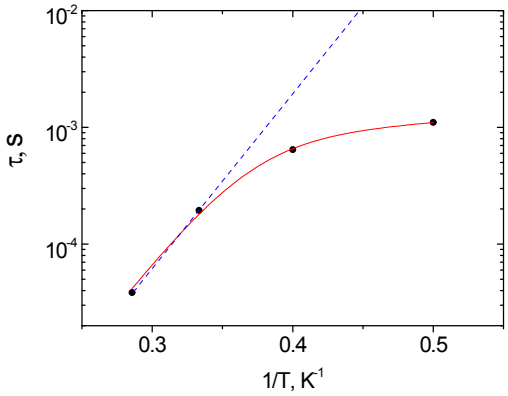


Fig. S23. τ vs. T^{-1} plot for **4Er** in 1000 Oe *dc*-field. Blue dashed line represents the best fit by the Arrhenius equation (Orbach mechanism). Red solid line represents the best fit by the sum of Orbach and direct mechanisms.

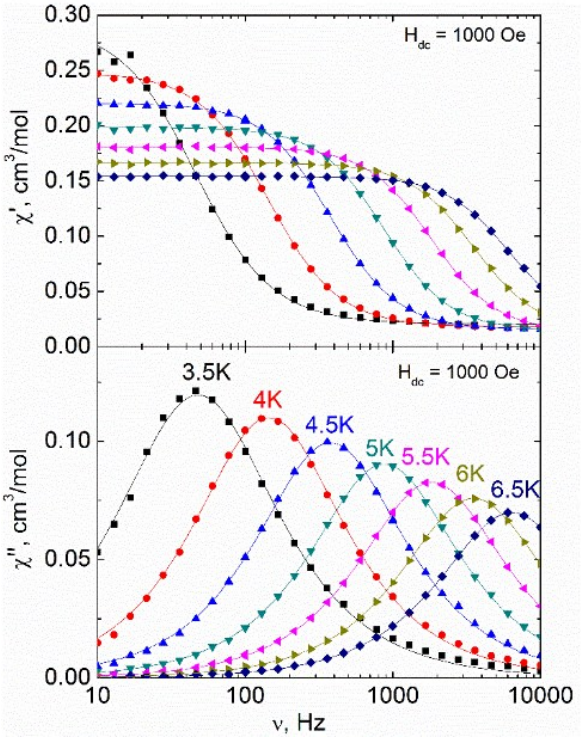


Fig. S24. Frequency dependencies of the real (χ', top) and imaginary (χ", bottom) components of the *ac* susceptibility between 3.5 and 6.5 K for **4Yb** in 1000 Oe *dc*-field. Solid lines were fitted using the generalized Debye model.

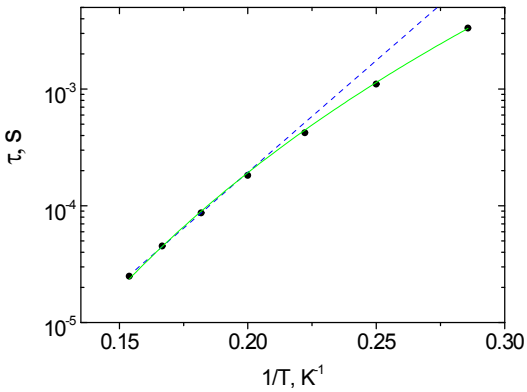


Fig. S25. τ vs. T^{-1} plot for **4Yb** in 1000 Oe *dc*-field. Blue dashed line represents the best fit by the Arrhenius equation (Orbach mechanism). Green solid line represents the best fit by the Raman mechanism.

Table S3. Results of the relaxation data approximation for the complexes with account for errors.

Complex		**1Er**	**1Yb**	**2Yb**	**3Yb**	**4Yb**	**5Yb**			**4Er**
Figure		Fig. S14	Fig. 4	Fig. S17	Fig. S19	Fig. 4	Fig. 4			Fig. S21
Raman	C, $K^{-n\_Raman}\cdot s^{-1}$	2.54×10^{-3} ($\pm2\times10^{-5}$)	440 (±6)	72.6 (±0.4)	0.061 (±0.001)	72.8 (±0.4)	0.59 (±0.02)	Raman	C, $K^{-n\_Raman}\cdot s^{-1}$	-
	n_{Raman}	**4.622 (±0.008)**	**8.55 (±0.01)**	**7.985 (±0.004)**	**4.53 (±0.03)**	**7.982 (±0.005)**	**5.16 (±0.05)**		n_{Raman}	-
	R_{Ram}	0.99875	0.9984	0.9997	0.99541	0.99972	0.98606		R_{Ram}	-
Orbach	Temperature range, K	2.8-3	5-7	6-7	4-5	5.5–6.5	6-7	Orbach	Temperature range, K	2.5-3.5
	Δ_{eff}/k_B, K	**14 (±1)**	**50 (±1)**	**47 (±1)**	**22 (±1)**	**44 (±1)**	**37 (±1)**		Δ_{eff}/k_B, K	**35 (±1)**
	τ_0, s	1.5×10^{-7} ($\pm1.8\times10^{-8}$)	2.3×10^{-8} ($\pm7.5\times10^{-9}$)	1.7×10^{-8}	4.5×10^{-7}	2.9×10^{-8}	8.4×10^{-8}		τ_0, s	2.0×10^{-9}
	R_{Or}	0.99998	0.99951	0.99893	0.99866	0.99951	0.99972		R_{Or}	1
Orbach + Raman	Δ_{eff}/k_B, K	**20 (±1)**	**56 (±1)**	**3 8(±1)**	**26 (±1)**	**40 (±1)**	**37 (±1)**	**Orbach+ direct**	Δ_{eff}/k_B, K	**35 (±1)**
	τ_0, s	2.0×10^{-7} ($\pm8.6\times10^{-8}$)	1.3×10^{-8} ($\pm3.7\times10^{-10}$)	4.5×10^{-7} ($\pm1.8\times10^{-7}$)	3.3×10^{-7} ($\pm3\times10^{-8}$)	2.3×10^{-7} ($\pm3.9\times10^{-8}$)	1.0×10^{-7} ($\pm1\times10^{-8}$)		τ_0, s	1.9×10^{-9} ($\pm1.3\times10^{-10}$)
	C, $K^{-n\_Raman}\cdot s^{-1}$	433 (±42)	2.74×10^{-2} ($\pm3\times10^{-4}$)	0.012 (±0.001)	34.3 (±0.7)	0.015 ($\pm8.5\times10^{-4}$)	3.8 (±0.2)		A_direct	4.5×10^{-10} ($\pm5.6\times10^{-12}$)
	n	4.5 (±0.2)	6.5 (±0.1)	7.9 (±0.1)	3.47 (±0.03)	7.8 (±0.1)	3.99 (±0.05)		n_direct	4*
	R_{Or_Ram}	0.99999	1	1	1	1	0.99977		R_{Or_dir}	0.99921

* $n_{\_direct}$ = 4 is set as a constant for Kramers systems.