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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 $[Ln(H_2O)_5(NCS)_3]$ ·H₂O (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), $[Ln(H_2O)(phen)_2(NCS)_3]$ ·phen·0.5H₂O (**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 Yb³⁺. 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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Table S1. Crystal data and structure refinement for the complex	xes.
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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)
Ζ	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	-12<=h<=12
	-10<=k<=10	-10<=k<=10
	-18<=1<=18	-18<=l<=18
Reflections collected	15215	14999
Independent reflections, Rint	5136, 0.0213	5103, 0.0220
Completeness to $\theta = 25.242^{\circ}$	99.9 %	99.9 %
Absorption correction	Semi-empirical	Semi-empirical
	from equivalents	from equivalents
Max,. min. transmission	0.2693, 0.1539	0.2693, 0.1826
Refinement method	Full-matrix	Full-matrix
_ / . /	least-squares on F ²	least-squares on F ²
Data / restraints / parameters	5136 / 13 / 183	5103 / 13 / 183
Goodness-of-fit	1.042	1.212
R1, wR2 [l>2sigma(l)]	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_bp y_2018_04_26.raw_1

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)

Inst	rume	ent						
Pr	imar	y radius (m	nm)		280			
Se	cond	ary radius	(mm)		280			
Li	near	PSD 2Th an	ngular range	(°)	2.94			
	FDS	angle (°)			0.8			
	Bea	m spill, sa	ample length	(mm)	20			
		Intensity o	corrected					
Corr	ecti	ons						
Sp	ecim	en displace	ement		0.22			
LP	P Fac	tor			0			
Misc	ella	aneous						
St	art	X			5			
Fi	nish	Х			50			
C +		. 1						
SLIU Dh	CLUI				[Exc(u20) (bpr	1) 2 (NICC) 21.0 5	(hpt) • 420
РП Р-	Brad	a			[EI(/ 1/	л20) (bp <u>y</u> 2	//2(NCS)5]•0.5	(рру) нго
Sr	bray	y roun			т.1т Р-1	2		
Sc	rale	roup				006249(3	38)	
Ce	ALC N	255			1536	000215(0	507	
Ce	211 V	olume (Å^3)			1538	.14(25)		
Wt	:8 -	Rietveld			100.	000		
Cr	vsta	l Linear Ab	sorption Coe	eff. (1/cm)	72.7	02(12)		
Cr	vsta	l Density ((q/cm^3)	, · · ,	1.65	825 (26)		
Pr	efer	red Orienta	ation (Dir 1	: 0 1 -1)	0.47	66(40)		
			(Dir 2	: 0 0 1)	0.77	28(66)		
	Fra	ction of Di	.r 1		0.44	0(10)		
PV	/II p	eak type						
	FWH	M = a + b/C	Cos(Th) + c 7	[an(Th)				
		a			0.02	80922		
		b			0.00	2285158		
	_	C			0.08	668674		
	Exp	onent m = (.6+ma+mb/Cos	s(Th)+mc/Tan	('I'h)			
		mb			0			
	•	mc			0 05	300037		
La	ttic	e parameter	ŝ		0.00	522257		
20	a (Å)			9.77	17(12)		
	b (Å)			12.9	8653 (96)	1	
	с (Å)			13.1	5957 (74)	1	
	alp	ha (°)			110.	9886(52)	1	
	bet	a (°)			94.3	831(80)		
	gam	ma (°)			96.1	82(11)		
<u>Site</u> Fr1	<u>Np</u> 2	X 0 15/87	<u> </u>	Z	Ato Er	<u>m Occ</u>	<u>Beq</u>	
91 21	2	0.13487	0.55298	0.10754	G LIT	1	1	
S2	2	0.53655	0 20377	-0 04743	S	1	1	
S3	2	-0.03347	0.24831	-0.23976	S	1	1	
01	2	0.18500	0.53052	0.15550	0	1	2	
Н1	2	0.26830	0.57840	0.17880	Н	1	4	
Н2	2	0.13250	0.58000	0.18790	Н	1	4	
02	2	0.42460	0.66770	0.21630	0	1	2	
НЗ	2	0.44110	0.70010	0.15740	Н	1	4	
H4	2	0.47310	0.72220	0.28280	Н	1	4	
N1	2	0.32790	0.46250	0.31450	Ν	1	2	
N2	2	0.34900	0.33170	0.06650	Ν	1	2	
NЗ	2	0.05590	0.30030	-0.01950	Ν	1	2	
N4	2	0.26530	0.20290	0.20600	Ν	1	2	
N5	2	-0.00330	0.17030	0.12510	Ν	1	2	
N6	2	0.05360	0.36010	0.34091	Ν	1	2	
N'/	2	-0.07820	0.42090	0.18890	N	1	2	
N8 C1	2	0.5/210	0.89/00	0.39650	N	⊥ 1	2	
U L	2	0.33/00	0.00090	0.30030	C	1	2	

C2	2	0.42720	0.28110	0.01840	С	1	2
C3	2	0.01990	0.27890	-0.11080	С	1	2
C4	2	0.40210	0.21930	0.23800	С	1	2
H4A	2	0.45530	0.28750	0.24430	Н	1	4
C5	2	0.46900	0.14060	0.26220	С	1	2
H5A	2	0.56610	0.15450	0.28500	Н	1	4
C6	2	0.39200	0.04280	0.25260	С	1	2
H6A	2	0.43510	-0.01300	0.26800	Н	1	4
C7	2	0.25240	0.02560	0.22050	С	1	2
H7A	2	0.19780	-0.04210	0.21440	Н	1	4
C8	2	0.19040	0.10670	0.19700	С	1	2
С9	2	0.04100	0.09200	0.15900	С	1	2
C10	2	-0.05000	0.00130	0.15540	С	1	2
H10A	2	-0.01730	-0.05270	0.18060	Н	1	4
C11	2	-0.18680	-0.01130	0.11600	С	1	2
H11A	2	-0.24970	-0.07310	0.11460	Н	1	4
C12	2	-0.23190	0.06600	0.07870	С	1	2
H12A	2	-0.32600	0.05830	0.04910	Н	1	4
C13	2	-0 13760	0 15570	0 08500	C	1	2
013 Н13Д	2	-0 16910	0 21000	0 05980	н	1	4
C14	2	0 12250	0.33220	0.41680	C	1	2
011 н14д	2	0.21580	0.31960	0 40910	н	1	Δ
C15	2	0.21500	0.32090	0.50560	C C	1	2
С15 Ц15Д	2	0.00070	0.30130	0.55780	с ц	1	2 Л
C16	2	-0 06930	0.33880	0.51650	C II	1	2
С10 Н16Д	2	-0 11200	0.33050	0.51620	с ц	1	 Л
C17	2	-0 1/160	0.36860	0.37020	II C	1	2
U177	2	-0.23500	0.38130	0.44070	U U	1	 Л
C18	2	-0.23300	0.38040	0.44700	II C	1	2
C10	2	-0.14810	0.11840	0.33300	C	1	2
C19 C20	2	-0.27670	0.41040	0.27200	C	1	2
	2	-0.27070	0.45470	0.20410		1	 Л
C21	2	-0.32440	0.45250	0.34360	п	1	4
	2	-0.33500	0.49390	0.20070	U	1	 л
C22	2	-0.42260	0.31920	0.21010	п	1	4
	2	-0.26480	0.49570	0.12300	C	1	2
HZZA	2	-0.30280	0.52180	0.06960	H	1	4
023	2	-0.13770	0.45870	0.11620	C	1	2
HZJA	2	-0.08930	0.46000	0.05660	H	1	4
C24	2	0.69470	0.8/930	0.35870	C	1	2
H24A	2	0.69860	0.81150	0.29980	Н		4
C25	2	0.81390	0.95340	0.40040	С	1	2
H25A	2	0.89870	0.93760	0.37160	H	1	4
C26	2	0.80810	1.05060	0.48450	С	1	2
H26A	2	0.88890	1.10440	0.51470	Н	1	4
C27	2	0.68360	1.07040	0.52560	С	1	2
H27A	2	0.67800	1.13750	0.58470	Н	1	4
C28	2	0.56790	0.99150	0.47970	С	1	2

File 1 : H:\SP_Er_Yb_NCS\Pow\2\Yb_NCS_bpy\Yb_NCS_bpy_2018_04_2 6.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 860(700) One on X 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 10 Sample length (mm) 3 Receiving Slit length (mm) Primary Sollers (°) 2.5 Secondary Sollers (°) 2.5 Corrections 0.1329832 Specimen displacement 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 0.0001581(12) Scale 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)0.000766512 а b 0.006068987 0.1576263 С Exponent m = 0.6 + ma + mb/Cos(Th) + mc/Tan(Th)0.06540861 ma mb 0.005475635

		mc			0.00	4191095	
La	ttic	e parameter	S				
	a (Å)			9.77	66(13)	
	b (Å)			12.9	8138(96)	
	с (Å)			13.1	4494 (82)	
	alp	ha (°)			110.	9527(57)	
	bet	a (°)			94.4	390 (88)	
	gam	ma (°)			95.9	765 (95)	
<u>Site</u>	Np	Х	У	Z	Ato	m 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
01	2	0.18500	0.53052	0.15550	0	1	2
H1	2	0.26830	0.57840	0.17880	Н	1	4
H2	2	0.13250	0.58000	0.18790	Н	1	4
02	2	0.42460	0.66770	0.21630	0	1	2
нЗ	2	0.44110	0.70010	0.15740	Н	1	4
H4	2	0.47310	0.72220	0.28280	Н	1	4
Nl	2	0.32790	0.46250	0.31450	Ν	1	2
N2	2	0.34900	0.33170	0.06650	Ν	1	2
NЗ	2	0.05590	0.30030	-0.01950	Ν	1	2
N4	2	0.26530	0.20290	0.20600	Ν	1	2
N5	2	-0.00330	0.17030	0.12510	Ν	1	2
NG	2	0.05360	0.36010	0.34091	Ν	1	2
N7	2	-0.07820	0.42090	0.18890	Ν	1	2
N8	2	0.57210	0.89700	0.39650	Ν	1	2
C1	2	0.39780	0.53890	0.38030	С	1	2
C2	2	0.42720	0.28110	0.01840	С	1	2
С3	2	0.01990	0.27890	-0.11080	С	1	2
C4	2	0.40210	0.21930	0.23800	С	1	2
H4A	2	0.45530	0.28750	0.24430	Н	1	4
С5	2	0.46900	0.14060	0.26220	С	1	2
H5A	2	0.56610	0.15450	0.28500	Η	1	4
C6	2	0.39200	0.04280	0.25260	С	1	2
H6A	2	0.43510	-0.01300	0.26800	Н	1	4
С7	2	0.25240	0.02560	0.22050	С	1	2
H7A	2	0.19780	-0.04210	0.21440	Н	1	4
С8	2	0.19040	0.10670	0.19700	С	1	2
С9	2	0.04100	0.09200	0.15900	С	1	2
C10	2	-0.05000	0.00130	0.15540	С	1	2
H10A	2	-0.01730	-0.05270	0.18060	Н	1	4
C11	2	-0.18680	-0.01130	0.11600	С	1	2
H11A	2	-0.24970	-0.07310	0.11460	Н	1	4
C12	2	-0.23190	0.06600	0.07870	С	1	2
H12A	2	-0.32600	0.05830	0.04910	Н	1	4
CI3	2	-0.13/60	0.15570	0.08500	С	1	2
HIJA	2	-0.16910	0.21000	0.05980	H	1	4
C14	2	0.12250	0.33220	0.41680	С	1	2
HI4A	2	0.21580	0.31960	0.40910	Н	1	4
	2	0.06570	0.32090	0.50560	C II	1	Δ
ALSA C16	2	0.11840	0.30130	0.55780	н	1	4
	2	-0.00930	0.33060	0.51050	U	1	Δ
C17	2	-0.11200	0.33030	0.37620	п	1	4
U177	2	-0.23500	0.30000	0.44070	U U	⊥ 1	ے ۸
п1/А С18	2	-0.23300	0.38040	0.44700	п	⊥ 1	4
C19	2	_0 1/210	0.30040	0.33300	C	⊥ 1	∠ 2
C20	2	-0 27670	0.41040	0.27200	C	⊥ 1	2
U20 H20A	2	-0 32440	0.45250	0.20410	с н	⊥ 1	∠ ⊿
C21	2	-0 33500	0 49390	0 20870	C	1	- 2
H21A	2	-0.42260	0.51920	0.21610	Ч	1	4
C22	2	-0.26480	0.49570	0.12300	C	- 1	2
H22A	2	-0.30280	0.52180	0.06960	н	1	4
C23	2	-0.13770	0.45870	0.11620	C	- 1	2
H23A	2	-0.08930	0.46000	0.05660	Н	1	4

4
2
4
2
4
2
4
2

3Er

File 1 :

S:\Andr\Paper\SP_Er_Yb_NCS\Pow\3\Er_NCS_phen\Er_NCS_p hen_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 Chebychev polynomial, Coefficient 0 1 2 3 4 5 6 7	8300(1300) -315(79) 523(82) -292(43) 159(22) -81(11) 41.5(60) -19.9(29) 12.7(17)
Instrument	
Primary radius (mm) Secondary radius (mm) Linear PSD 2Th angular range (°) FDS angle (°) Beam spill, sample length (mm) Intensity corrected	280 280 2.94 0.9 30
Corrections Specimen displacement LP Factor	0.2022206 0
Miscellaneous	
Start X Finish X	5 50
Structure 1	
<pre>Phase name Phase name R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) PVII peak type FWHM = a + b/Cos(Th) + c Tan(Th)</pre>	<pre>[Er(H2O)(phen)2(NCS)3]•phen•0.5H2O 2.509 P-1 0.00004059(19) 1818.328 1860.03(23) 100.000 61.2126(77) 1.62331(20)</pre>

		a b			0.00	9437339 041474	
		С			0.18	93084	
	Exp	oonent m = 0 ma	.6+ma+mb/Cos	s(Th)+mc/Tan	(Th) 0		
		mb			0		
To	++-	mc	-		0.06	1891	
Lа	a	(Å)	5		10.4	2599(65)	
	b	(Å)			12.6	7156(94)	
	С	(Å)			15.2	792(10)	
	alp bot	oha (°)			96.7 104	453 (54)	
	gan	nma (°)			104.	6756(63)	
Site	Np	х	V	Z	Ato	m 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
01	2	0.13343	0.44630	0.38580	0	1 1	2
H1	2	0.42490	0.44490	0.08750	H	1	4
Н2	2	0.41310	0.51260	0.16250	Н	1	4
021	2	0.49800	0.57930	0.02910	0	0.25	2
H101	2	0.45580	0.60750	-0.01360	Н	0.25	4
H1UZ	2	0.53350	0.61620	0.08400	H	0.25	4
H112	2	0.58670	0.59470	0.09120	Н	0.25	4
H110	2	0.49570	0.59440	0.01620	Н	0.25	4
N1	2	0.62070	0.23390	0.31410	Ν	1	2
N2	2	0.62190	0.33400	0.13400	Ν	1	2
N3	2	0.29310	0.15510	0.27140	N	1	2
N4 N5	2	0.51960	0.39370	0.30390	N	⊥ 1	2
N6	2	0.23110	0.21820	0.06550	N	1	2
N7	2	0.41480	0.09860	0.11920	Ν	1	2
N8	2	0.61250	0.70150	0.20760	Ν	1	2
N9	2	0.33720	0.63710	0.19930	N	1	2
CI C2	2	0.72340	0.22/80	0.36160	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	Н	1	4
С5	2	0.11570	0.42210	0.34400	С	1	2
H5A	2	0.01950	0.39490	0.33620	H	1	4
С6 Н6Д	2	0.18930	0.51920	0.40120	с н	1	∠ 4
C7	2	0.33130	0.55770	0.41250	C	1	2
C8	2	0.41540	0.66040	0.47180	С	1	2
H8A	2	0.37370	0.70520	0.50430	Н	1	4
C9	2	0.55080	0.69350	0.48160	С	1	2
C10	2	0.60350	0.76150	0.52120	н С	1	4
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	С	1	2
H12A	2	0.91190	0.61860	0.40150	Н	1	4
C13	2	0.73170	0.49760	0.34000	С	1	2
пт3А С14	2	U.//29U N 53910	U.4318U 0 52900	U.JUXIU A 37500	н С	⊥ 1	4
C15	2	0.39300	0.49240	0.36320	C	_ 1	2
C16	2	0.14060	0.27510	0.03930	С	1	2
H16A	2	0.15510	0.34590	0.07480	Н	1	4
C17	2	0.02450	0.23640	-0.03810	С	1	2
H17A	2	-0.03800	0.27980	-0.05410	H	1	4
010 H18A	∠ 2	-0.07450	0.10750	-0.14330	с Н	⊥ 1	∠ 4

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

File 1 :

S:\Andr\Paper\SP_Er_Yb_NCS\Pow\3\Yb_NCS_phen\Yb_NCS_p hen 2018 04 04.raw 1

Range Number : 1

R-Values

Rexp: 5.97Rwp: 8.28Rp : 6.58GOF : 1.39Rexp`: 11.53Rwp`: 15.98Rp` : 13.66DW : 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, Coe	efficient O	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 of	corrected				
Corr	ect	ions					
Sp	ecim	en displace	ement		0 334	9183	
LP	' Fac	tor			0.001	9105	
Misc	ella	aneous					
St	art	Х			5		
Fi	nish	ı X			50		
0+	-	. 1					
Stru	Ctu	re 1			[Vh/[(20) (phon)	$2(NCS)$ $31 \cdot nhon \cdot 0$ 5420
R-	Brac	nanie			2 294	(pileii)	2 (NCS) 5] • phen • 0 • 51120
Sp	acec	roup			P-1	-	
Sc	ale				0.000	02764(19)	
Ce	11 M	lass			1829.	887	
Ce	ell V	Olume (A^3))		1850.	12(32)	
Cr	vsta	l Linear At	osorption Coe	off (1/cm)	66 46	53 (11)	
Cr	ysta	l Density	(g/cm^3)	(1) (1)	1.642	238 (28)	
Pr	efer	red Orienta	ation Spheric	cal Harmonics			
	Ord	ler			2		
	y00)			1) (1 E)	
	y20 v21	m			0.009	(13)	
	y21	.n.			0.022	2(12)	
	y22	2m			0.004	(14)	
	y22	2p			0.088	8(13)	
PV	'II p Ewr	eak type		nan (Th)			
	L' VVI.	a - a - b/(.03(111) - C 1		0.004	810939	
		b			0.005	862314	
		С	/		0.259	0598	
	Exp	onent m = ().6+ma+mb/Cos	s(Th)+mc/Tan(Th)		
		mb			0		
		mc			0.041	34817	
La	ttic	e parameter	rs				
	a (Å)			10.40	415(84)	
	b ((A)			12.65	62(13)	
	alr	A) bha (°)			96 81	15(73)	
	bet	a (°)			105.1	.554(71)	
	gan	uma (°)			103.6	5804(84)	
<u>Site</u> vh1	<u>Np</u> 2	X 0 44470	<u> </u>	<u> </u>	Atom vh	1 0CC	<u>Beq</u>
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
01	2	0.40480	0.44630	0.13910	0	1	2
HL H2	2	0.42490	0.44490	0.08/50	H H	⊥ 1	4
021	2	0.49800	0.57930	0.02910	0	0.25	2
H101	2	0.45580	0.60750	-0.01360	H	0.25	4
H102	2	0.53350	0.61620	0.08400	Н	0.25	4
022	2	0.55600	0.56030	0.03540	0	0.25	2
HIIZ H110	2	0.58670	0.59470	0.09120	H 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
NЗ	2	0.29310	0.15510	0.27140	Ν	1	2
N4	2	0.31960	0.39570	0.30590	N	1	2
N5 N6	2	U.59690 0 23110	U.4644U 0 21820	U.32880 0 06550	N N	⊥ 1	2
N7	2	0.41480	0.09860	0.11920	N	1	2

N8	2	0.61250	0.70150	0.20760	Ν	1	2
NG	2	0 33720	0 63710	0 10030	NT	1	2
	2	0.33720	0.03710	0.19930	IN	1	~
C1	2	0.72340	0.22780	0.36160	С	1	- 2
C2	2	0 71910	0 37880	0 11480	C	1	2
a 2	-	0.0000	0 10720	0.21070	a	- 1	-
03	Ζ	0.23600	0.10/30	0.318/0	C	T	Z
C4	2	0.18500	0.36270	0.29640	С	1	2
ц / ъ	2	0 13290	0 29550	0 25550	ц	1	Λ
11-171	2	0.13230	0.29000	0.23330	11	1	-
C5	2	0.115/0	0.42210	0.34400	С	\perp	2
H5A	2	0.01950	0.39490	0.33620	Н	1	4
00	2	0 10020	0 51020	0 40120	~	1	2
60	2	0.18930	0.51920	0.40120	C	T	2
H6A	2	0.14450	0.56110	0.43360	Н	1	4
C7	2	0 33130	0 55770	0 /1250	C	1	2
07	2	0.00100	0.00770	0.41250	0	1	~
C8	2	0.41540	0.66040	0.47180	С	1	2
H8A	2	0.37370	0.70520	0.50430	Н	1	4
<u> </u>	2	0 55000	0 60250	0 10160	C	1	2
09	Ζ	0.55060	0.09330	0.40100	C	T	2
H9A	2	0.60350	0.76150	0.52120	Н	1	4
C10	2	0 61780	0 63020	0 43460	C	1	2
010	-	0.010	0.00020	0.10100	â	-	2
CII	2	0./6010	0.66140	0.44430	С	\perp	2
H11A	2	0.81680	0.72790	0.48440	Н	1	4
C12	2	0 81610	0 59690	0 30670	C	1	2
	2	0.01010	0.59090	0.39070	C	1	~ ~
H12A	2	0.91190	0.61860	0.40150	Н	1	4
C13	2	0 73170	0 49760	0 34000	С	1	2
010 1127	-	0.77000	0.45100	0.20010		1	~
HI 3A	2	0.//290	0.45180	0.30810	Н	T	4
C14	2	0.53940	0.52900	0.37500	С	1	2
C15	2	0 30300	0 19210	0 36320	C	1	2
	2	0.55500	0.49240	0.30320	0	1	2
C16	2	0.14060	0.27510	0.03930	С	1	2
H16A	2	0.15510	0.34590	0.07480	Н	1	4
017	2	0.00450	0.02000	0 0 2 0 1 0	~	1	2
CI/	Ζ	0.02450	0.23640	-0.03810	C	T	Z
H17A	2	-0.03800	0.27980	-0.05410	Н	1	4
C18	2	0 00290	0 13480	-0 09020	C	1	2
010 11107	2	0.00290	0.10750	0.00020		1	~
HI8A	2	-0.0/450	0.10/50	-0.14330	Н	T	4
C19	2	0.09480	0.07140	-0.06500	С	1	2
C20	2	0 07810	-0 03460	-0 11530	C	1	2
C20	2	0.07010	-0.03400	-0.11550	C	1	~ ~
H20A	2	0.00400	-0.06340	-0.17030	Н	1	4
C21	2	0.16650	-0.09600	-0.08610	С	1	2
UD17	2	0 1 5 0 0 0	0 1 (7 2 0	0 10000		1	
HZIA	2	0.15220	-0.16/30	-0.12060	н	T	4
C22	2	0.27870	-0.05570	-0.00570	С	1	2
C23	2	0 37210	-0 11570	0 02610	C	1	2
020	2	0.07210	0.10000	0.02010		1	~
HZ3A	2	0.35870	-0.18860	-0.00500	Н	T	4
C24	2	0.48240	-0.07000	0.10160	С	1	2
U217	2	0 51590	-0 11060	0 12/10	U	1	Л
112 46	2	0.54550	0.11000	0.12410	-	1	-
C25	2	0.50070	0.03850	0.14570	С	1	2
H25A	2	0.57920	0.07030	0.19740	Н	1	4
C26	2	0 20400	0 05250	0 04470	C	1	2
C20	2	0.30400	0.03230	0.04470	C	T	2
C27	2	0.20820	0.11650	0.01490	С	1	2
C28	2	0.74620	0.73240	0.21430	С	1	2
11007	2	0 70200	0 (0(0)	0 17020		1	_
п∠оА	Ζ	0.70200	0.00000	0.1/020	п	T	4
C29	2	0.83520	0.82800	0.27150	С	1	2
Н29А	2	0 93040	0 84630	0 27440	н	1	4
a20	-	0.70000	0.00500	0.00070	~	1	_
030	2	0./8620	0.89580	0.32370	C	T	Z
H30A	2	0.84670	0.96180	0.36260	Н	1	4
C31	2	0 64620	0 86720	0 31920	C	1	2
~~~	2	0.04020	0.00720	0.01020	ĉ	1	2
C32	2	0.58660	0.934/0	0.36840	С	$\perp$	2
H32A	2	0.64410	1.00110	0.40840	Н	1	4
C 2 2	2	0 11060	0 00720	0 26000	C	1	2
035	2	0.44900	0.90720	0.30000	C	1	2
H33A	2	0.41200	0.95490	0.39320	Н	1	4
C34	2	0.36090	0.80700	0.30160	С	1	2
02F	2	0 01050	0 77400	0 20200	Ċ	-	-
53	2	0.21930	0.//460	0.29280	C	T	2
H35A	2	0.17860	0.82020	0.32510	Η	1	4
C36	2	0 14070	0 67670	0 23750	С	1	2
1126-	1	0.01100	0.07070	0.00000	~	± 1	~
нзюА	Ζ	∪.∪44∠U	U.6339U	0.22990	Н	$\perp$	4
C37	2	0.20400	0.61130	0.19240	С	1	2
НЗЛ⊅	2	0 14770	0 54350	0 15410	н	1	Л
11.J / A	2	0.11550	0.04000	0.10110	~	± 1	
C38	2	0.41550	0.73570	0.25250	С	$\perp$	2
C39	2	0.56220	0.76680	0.25990	С	1	2

# File 1 : G:\Andr\Paper\SP_Er_Yb_NCS\Pow\4\Er_NCS_bpy_HNCS\Er_N CS_bpy_HNCS_2018_04_25.raw_1 Range Number : 1

#### **R-Values**

Rexp: 4.37Rwp: 8.09Rp : 5.75GGRexp`: 8.93Rwp`: 16.51Rp` : 13.39DV	DF : 1.85 V : 1.17
Number of independent parameters : 14	
Quantitative Analysis - Rietveld Phase 1 : [Hbpy][Er(NCS)4(bpy)2]	100.000 %
Background One on X Chebychev polynomial, Coefficient 0 1 2 3 4 5	D(510) 295(32) -15(33) -10(17) -14.8(88) 8.8(42) -8.6(25)
<pre>Instrument Primary radius (mm) Secondary radius (mm) Linear PSD 2Th angular range (°) FDS angle (°) Beam spill, sample length (mm) Intensity corrected</pre>	280 280 2.94 1.2 18
Corrections Specimen displacement	0.2324584
LP Factor	0
Miscellaneous	_
Start X Finish X	5
bhl Dhaca 1 Iabail mathad	50
<pre>hkl Phase - 1 Lebail method Phase name R-Bragg Spacegroup Cell Mass Cell Volume (Å^3) Wt% - Rietveld Cruatallite Size</pre>	[Hbpy][Er(NCS)4(bpy)2] 0.957 P-1 1738.31 1795.66(13) 100.000
Cry size Lorentzian (nm) PV_MOD peak type: a + b Tan(Th) + c / Cos FWHM a b c Lorentzian mix a b c Lattice parameters a (Å) b (Å)	190.8(28) (Th) 0.0001000024 0.0746289 0.0001000024 0.0001000024 0.212323 0.0001000024 9.65697(39)
D (A) C (Å) alpha (°) beta (°) gamma (°)	16.30576(63) 112.3937(28) 94.5259(37) 107.8103(32)

#### File 1 : G:\Andr\Paper\SP_Er_Yb_NCS\Pow\4\Yb NCS bpy HNCS\Yb N CS bpy HNCS 2018 04 25.raw 1 Range Number : 1 **R-Values** Rwp : 8.59Rp : 5.86GOF : 2.88Rwp : 18.44Rp : 14.53DW : 1.15 Rexp : 2.98 Rexp`: 6.39 Quantitative Analysis - Rietveld Phase 1 : [Hbpy] [Yb(NCS) 4(bpy) 2] 100.000 % Background Chebychev polynomial, Coefficient 0 675.4(22) 167.0(37) 1 2 6.2(34) 3 -39.4(33)28.4(30)4 5 -21.8(30)Instrument 280 Primary radius (mm) Secondary radius (mm) 280 Linear PSD 2Th angular range (°) 2.94 FDS angle (°) 1.2 Beam spill, sample length (mm) 18 Intensity corrected Corrections -0.0009435189 Specimen displacement 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 0.01439521 С Lorentzian mix a 0.8456502 b 0.0001 0.3323685 С 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)

File 1 : S:\Andr\Paper\SP_Er_Yb_NCS\Po	w\5\Er_NCS_phen_HNCS\Er_
Range Number : 1	_±
R-Values	
Rexp: 2.92Rwp: 7.26Rp : 5.64Rexp`: 3.27Rwp`: 8.12Rp`: 7.05	GOF : 2.48 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 Chebychev polynomial, Coefficient 0 1 2 3 4 5 6 7	9200(1900) 70(140) 660(150) -469(84) 207(47) -94(26) 45(15) -31.8(75) 55.1(48)
<pre>Instrument Primary radius (mm) Secondary radius (mm) Linear PSD 2Th angular range (°) FDS angle (°) Beam spill, sample length (mm) Intensity corrected</pre>	280 280 2.94 1 25
<b>Corrections</b> Specimen displacement LP Factor	0.2 0
Miscellaneous	
Start X Finish X	4 50
Structure 1 Phase name	[Hphen][Er(NCS)4(phen)2]
<pre>R-Bragg Spacegroup Scale Cell Mass Cell Volume (Å^3) Wt% - Rietveld Crystal Linear Absorption Coeff. (1/cm) Crystal Density (g/cm^3) Preferred Orientation (Dir 1 : 1 -1 -1)</pre>	3.933 P21/n 0.00002210(12) 3764.933 3873.24(35) 100.000 63.7363(58) 1.61411(15) 0.5756(51) 0.674(12) 0.693(19) s(Th)

0.04(43)

0.5(50)

0.24(99) 0.1(50)

12.44936(54)

0.083(80) 0.04(43)

-FWHM a

a (Å)

b

С

Lattice parameters

Lorentzian mix a

b

С

(Å)		
(Å)		
ta	(°)	
	(Å) (Å) ta	(Å) (Å) ta (°)

Site	Np	x	V	7.	Ator		Bea
<u>s_cc</u> 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
92	Δ	0.66095	-0 05586	0 45204	g	1	1
SJ SJ	1	0.000000	-0.03896	0.10436	c c	1	1
N1	1	0.72213	0.03030	0.25352	N	1	2
N2	л Л	0.72213	0.15324	0.20002	N	⊥ 1	2
	7	0.50007	0.13324	0.32170	IN NT	1	2
N J N 4	4	0.30013	0.07370	0.30070	IN NT	1	2
N4 NE	4	0.49369	0.0/428	0.20809	IN N	1	2
CN	4	0.54/46	0.24790	0.40855	IN	1	2
N6	4	0.67062	0.30/9/	0.304/1	N	1	2
N /	4	0.43/0/	0.31657	0.26/3/	IN	1	2
N8	4	0.55056	0.24397	0.16469	N	1	2
N9	4	0.69372	0.08338	0.5/529	N	Ţ	2
Hl	4	0.71500	0.05630	0.53630	Н	1	4
N10	4	0.81207	0.15041	0.47210	Ν	1	2
C1	4	0.81170	0.14556	0.23681	С	1	2
C2	4	0.28060	0.17089	0.33912	С	1	2
С3	4	0.61911	0.02041	0.40218	С	1	2
C4	4	0.46783	0.02686	0.16507	С	1	2
C5	4	0.49200	0.21745	0.46062	С	1	2
H5A	4	0.46320	0.16400	0.45530	Н	1	4
C6	4	0.47350	0.25985	0.52307	С	1	2
НбА	4	0.43290	0.23560	0.55910	Н	1	4
C7	4	0.51450	0.33656	0.53152	С	1	2
H7A	4	0.50140	0.36680	0.57310	Н	1	4
C8	4	0.57610	0.37050	0.47873	С	1	2
С9	4	0.62600	0.44941	0.48467	С	1	2
H9A	4	0.61540	0.48160	0.52560	Н	1	4
C10	4	0.68730	0.47858	0.43365	С	1	2
H10A	4	0.71920	0.53100	0.43910	Н	1	4
C11	4	0.70560	0.43257	0.37152	С	1	2
C12	4	0.77180	0.45955	0.31798	С	1	2
H12A	4	0.80560	0.51150	0.32160	Н	1	4
C13	4	0.78770	0.41156	0.26104	С	1	2
H1.3A	4	0.83310	0.42920	0.22480	Н	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
017 Н17Д	4	0 35680	0 32010	0 35440	н	1	4
C18	4	0.33990	0 43229	0 30994	C	1	2
H18A	4	0 29520	0 45430	0 34490	н	1	4
C19	1	0.36960	0.17861	0.25420	C	1	2
н19д	Δ	0 34770	0 53400	0.25080	н	1	2 4
C20	1	0.13230	0.00400	0.20000	C	1	2
C21	л Л	0.45250	0.19919	0.20205	C	1	2
U21 И21Д	л Л	0.40000	0.40010	0.13730	с ц	1	2
C22	7	0.52410	0.15267	0.13730	C II	⊥ 1	7
U22 U227	4	0.52410	0.45507	0.05242	U U	⊥ 1	2
022A	4	0.54090	0.40510	0.00570	C II	⊥ 1	
C23	4 /	0.55220	0.30000	0.05052	C	⊥ 1	2
U24 U247	4 1	0.00000	0.32043	0.043/9		⊥ 1	∠
н∠4А сог	4	0.02/20	0.33710	0.00290	н	1	4
025	4	0.63020	0.24/69	0.05122	C	1	2
ндра	4	0.00520	0.21900	U.U1500	H	1	4
026	4	0.60190	0.20/89	U.1133/	C	1	2
H26A	4	0.62050	0.15210	0.11890	H	1	4
C27	4	0.52280	0.32368	0.15595	С	1	2
C28	4	0.46294	0.36177	0.20975	С	1	2
C29	4	0.63590	0.04593	0.62260	С	1	2
H29A	4	0.61410	-0.00900	0.61510	Н	1	4

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

## 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

R-Bragg Spacegroup

Start X	4
Finish X	50
Structure 1	
Phase name	[Hphen][Yb(NCS)4(phen)2]
R-Bragg	3.174

Sc Ce Wt Cr Cr Pr	ale ell I ell V eysta cysta cefe: Fra	Mass Volume (Å^3) Rietveld al Linear Ak al Density rred Orienta action of Di	) (g/cm^3) ation (Dir 1 (Dir 2 ir 1	eff. (1/cm) : 1 -1 -1) : 0 1 0)	0.00 3788 3862 100. 68.6 1.62 0.74 0.67 0.85	0010700( .049 .45(32) 000 296(56) 855(13) 33(64) 2(39) 3(32)	60)
PV	/II ]	peak type					
	FWI	HM = a + b/0	Cos(Th) + c I	'an (Th)	0 00	0147076	
		a h			0.00	914/2/6 198601	
		C C			0.02	5215139	
	Ex	ponent m = (	).6+ma+mb/Cos	(Th)+mc/Tan	(Th)		
		ma			0.13	47203	
		mb			0.00	9668545	
La	tti	IIIC re parameter	rs		0.04	005351	
10	a	(Å)			12.4	4280(49)	
	b	(Å)			16.5	9188(76)	
	С	(Å)			18.7	246(10)	
	be	ta (°)			92.3	426(38)	
Site	Nη	x	V	7.	At∩	m Occ	Rea
<u>Yb1</u>	4	0.55090	0.17621	0.28812	Yb	1	<u></u> 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
NL N2	4	0.72213	0.144/3	0.20302	N N	1 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	Ν	1	2
N6	4	0.67062	0.30797	0.30471	Ν	1	2
N7	4	0.43707	0.31657	0.26737	Ν	1	2
N8	4	0.55056	0.24397	0.16469	N	1	2
N9 H1	4 4	0.69372	0.08338	0.57529	N H	1	ے م
N10	4	0.81207	0.15041	0.47210	N	1	2
C1	4	0.81170	0.14556	0.23681	С	1	2
C2	4	0.28060	0.17089	0.33912	С	1	2
C3	4	0.61911	0.02041	0.40218	С	1	2
C4	4	0.46783	0.02686	0.16507	C	1	2
U5 7	4 1	0.49200	0.21745	U.46U62	C u	⊥ 1	2
пја Сб	4	0.47350	0.25985	0.52307	п С	1	4 2
H6A	4	0.43290	0.23560	0.55910	H	1	4
С7	4	0.51450	0.33656	0.53152	С	1	2
H7A	4	0.50140	0.36680	0.57310	Н	1	4
C8	4	0.57610	0.37050	0.47873	С	1	2
C9 1107	4	0.62600	0.44941	0.48467	C	1	2
C10	4 4	0.01040	0.4010U 0.47858	0.02000	п С	⊥ 1	4
H10A	4	0.71920	0.53100	0.43910	H	_ 1	2 4
C11	4	0.70560	0.43257	0.37152	C	1	2
C12	4	0.77180	0.45955	0.31798	С	1	2
H12A	4	0.80560	0.51150	0.32160	Н	1	4
C13	4	0.78770	0.41156	0.26104	С	1	2
HI3A C14	4 1	0.83310	0.42920	0.22480	H	⊥ 1	4
ст4 н14д	4 4	U./36U8 0 74860	0.33578 0.30240	0.2364/ 0.21660	Ч	⊥ 1	∠ ∆
C15	4	0.65672	0.35501	0.36266	C	- 1	
C16	4	0.59155	0.32392	0.41737	C	1	2
C17	4	0.37659	0.35153	0.31476	С	1	2
H17A	4	0.35680	0.32010	0.35440	Н	1	4

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



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









**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 H₂O before 75°C. In the case of **2Er** and **2Yb**, the loss of coordinated H₂O 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	Coloulated avanall	Mass loss in a TGA experiment, wt. %*						
	H ₂ O content, wt. %	Coordinated H ₂ O	Outer-sphere H ₂ O	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	-				
<b>3Yb</b> 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  $[Yb(H_2O)(bpy)_2(NCS)_3]$ ·0.5bpy·H₂O samples.



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



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



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



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



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



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



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



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



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



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



**Fig. S15.** Frequency dependence of the real ( $\chi'$ , left) and imaginary ( $\chi''$ , 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.**  $\tau$  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 ( $\chi'$ , top) and imaginary ( $\chi''$ , 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 ( $\chi'$ , left) and imaginary ( $\chi''$ , 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.**  $\tau$  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 ( $\chi'$ , left) and imaginary ( $\chi''$ , 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.**  $\tau$  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 ( $\chi'$ , left) and imaginary ( $\chi''$ , 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.**  $\tau$  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 ( $\chi'$ , top) and imaginary ( $\chi''$ , 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.**  $\tau$  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.

Complex		1Er	1Yb	2Ŷb	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 (±2×10 ⁻⁵ )	440 (±6)	72.6 (±0.4)	0.061 (±0.001)	72.8 (±0.4)	0.59 (±0.02)	Raman	C, K ^{-n_Raman} ·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
	$\Delta_{\rm eff}/k_{\rm B},{\rm K}$	14 (±1)	50 (±1)	47 (±1)	22 (±1)	44 (±1)	37 (±1)		$\Delta_{\rm eff}/k_{\rm B},{\rm K}$	35 (±1)
	τ ₀ , s	1.5×10 ⁻⁷ (±1.8×10 ⁻ ⁸ )	2.3×10 ⁻ ⁸ (±7.5×10 ⁻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	$\Delta_{\rm eff}/k_{\rm B},{\rm K}$	20 (±1)	56 (±1)	3 8(±1)	26 (±1)	40 (±1)	37 (±1)	Orbach+ direct	$\Delta_{\rm eff}/k_{\rm B},{\rm K}$	35 (±1)
	τ ₀ , s	2.0×10 ⁻⁷ (±8.6×10 ⁻⁸ )	1.3×10 ⁻⁸ (±3.7×10 ⁻¹⁰ )	4.5×10 ⁻⁷ (±1.8×10 ⁻⁷ )	3.3×10 ⁻⁷ (±3×10 ⁻⁸ )	2.3×10 ⁻⁷ (±3.9×10 ⁻⁸ )	1.0×10 ⁻⁷ (±1×10 ⁻⁸ )		τ ₀ , s	1.9×10 ⁻⁹ (±1.3×10 ⁻¹⁰ )
	C, $K^{-n}Raman \cdot s^{-1}$	433 (±42)	2.74×10 ⁻² (±3×10 ⁻⁴ )	0.012 (±0.001)	34.3 (±0.7)	0.015 (±8.5×10 ⁻⁴ )	3.8 (±0.2)		A_direct	4.5×10 ⁻¹⁰ (±5.6×10 ⁻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

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

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