Electronic Supplementary Information

Table S1. Selected structural data of I and Ia

	I	Ia
Chemical formula	$C_{14}H_{32}ErN_{11}O_{12}$	$C_{16}H_{46}N_{14}O_{19}Th$
M_r	713.76	970.71
Crystal system	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
T / K	100	100
a, b, c (Å), β	14.749(3), 10.683(2), 15.594(3), 92.30(2)°	18.525 (4), 8.827 (1), 21.485 (4), 104.50 (2)
V (Å^3)	2455.2(1)	3401.3 (1)
Z	4	4
M / mm^{-1}	3.50	4.48
Crystal size / mm	0.31 × 0.20 × 0.07	0.41 × 0.35 × 0.03
No. of measured, independent and observed [I>2σ(I)] reflections	16035, 5980, 4940	15646, 7886, 6252
R_{int}	0.038	0.043
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650	0.681
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.104, 1.06	0.041, 0.101, 0.99
No. of reflections	5630	7886
No. of parameters	351	481
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.06, −1.22	3.26, −1.90

Table S2. Crystal field levels and the crystal field splitting (Δ_{CFS}) in cm^{-1} of the selected multiplets for $4f^{11}$ configuration in I and Ia¹ at 4.2 K

	$[ErEDTA(CO_3)]^{3-}$	$[ErEDTA(H_2O)_2]^{-}$		$[ErEDTA(CO_3)]^{3-}$	$[ErEDTA(H_2O)_2]^{-}$
$^4G_{11/2}$	26524	26596	$^4I_{9/2}$	12653	12685
	26494	26560		12646	12659
	26440	26511		12613	12555
	26353	26417		12491	12470
	26288	26330		12454	12392
	26272	26309		12384	
Δ_{CFS}	**252**	**287**	Δ_{CFS}	**269**	**293**
$^4F_{7/2}$	20603	20659	$^4I_{11/2}$	10312	10362
	20578	20612		10283	10352
	20570	20587		10259	10339
	20527	20534		10239	10313
	20484				10292
Δ_{CFS}	**119**	**125**	Δ_{CFS}	**73**	**70**
$^2H_{11/2}$	19283	19340	$^4I_{13/2}$	6774	6823
	19241	19298		6752	6787
	19223	19281		6733	6749
	19173	19225		6722	6681
	19125	19163		6709	6649
	19092	19126		6663	6585
Δ_{CFS}	**191**	**214**		6628	6577
				6569	
$^4S_{3/2}$	18428	18450		6556	
	18417	18424	Δ_{CFS}	**218**	**246**
	18371				
Δ_{CFS}	**57**	**26**			
$^4F_{9/2}$	15430	15479			
	15421	15408			
	15361	15370			
	15323	15316			
	15278	15278			
	15254				
	15251				
Δ_{CFS}	**179**	**201**			

Table S3. Oscillator strengths ($P \cdot 10^8$) and Ω_λ parameter values for I and Ia crystals (P values of hypersensitive transitions are in bold)

	$[Er(EDTA)(CO_3)]^{3-}$		$[Er(EDTA)(H_2O)_2]^-$	
$^4I_{15/2}\rightarrow$	$P_{exp}\cdot10^8$	$P_{calc}\cdot10^8$	$P_{exp}\cdot10^8$	$P_{calc}\cdot10^8$
$(^2H,^2G)_{9/2}$	50.5	35.4	55.6	19.4
$^2K_{15/2},^2G_{7/2}$	131.1	108.0	132.1	112.6
$^4G_{9/2}$	210.7	171.2	103.8	129.6
$^4G_{11/2}$	**1368.9**	1403.2	**700.4**	663.1
$(^2G,^4F,^2H)_{9/2}$	84,5	749.5	79.8	101.8
$^4F_{3/2},^4F_{5/2}$	106.1	99.1	139.3	136.6
$^4F_{7/2}$	211.6	221.6	258.0	257.0
$^2H_{11/2}$	**852.6**	792.4	**308.4**	375.5
$^4S_{3/2}$	75.2	51.9	61.4	71.3
$^4F_{9/2}$	215.7	248.9	226.5	210.6
$^4I_{9/2}$	42.2	43.7	17.6	25.5
$^4I_{11/2}$	46.6	64.8	77.6	76.8
$\Omega_2\cdot10^{20}$ /cm^2		4.96±0.14		2.11±0.24
$\Omega_4\cdot10^{20}$ /cm^2		2.14±0.11		1.17±0.37
$\Omega_6\cdot10^{20}$ /cm^2		1.40±0.19		1.93±0.22
rms$\cdot10^7$		3.21		3.19

Intensity of f-f transitions for I and Ia

The Judd-Ofelt[2,3] intensity analysis of f-f transitions was used for determination of Ω_λ parameters (Eqn 13 in Experimental section in the main text)

Among three Ω_λ parameters, the Ω_2 values are strongly influenced by the hypersensitive transitions intensities. This parameter is particularly sensitive to the polarizability of the coordinated ligands,[4] covalent[5], and vibronic effects,[6] while Ω_4 and Ω_6 are rather dependent on covalent interactions, the crystal field effects[7] as well as rigidity of the system.[8] The substitution of water molecules by more polarizable, bidendate CO_3^{2-} anion brings about a significant increase in intensities of the hypersensitive $^4I_{15/2} \rightarrow {}^4G_{11/2}$ and $^4I_{15/2}\rightarrow {}^2H_{11/2}$ transitions, as well as Ω_2 and Ω_4 parameter values. The polarizability of CO_3^{2-} anion (α_{CO_3} = 3.85 Å^3) is about 2.7 times higher than this of water (α_{H_2O}= 1.442 Å^3).[9] The Ω_6 parameter value is smaller in I than in Ia and it is probably because of higher rigidity[9] of $[Er(EDTA)(CO_3)]^{3-}$ complex in comparison with the hydrated $[Er(EDTA)(H_2O)_2]^-$ one as it was shown in crystal structure section.

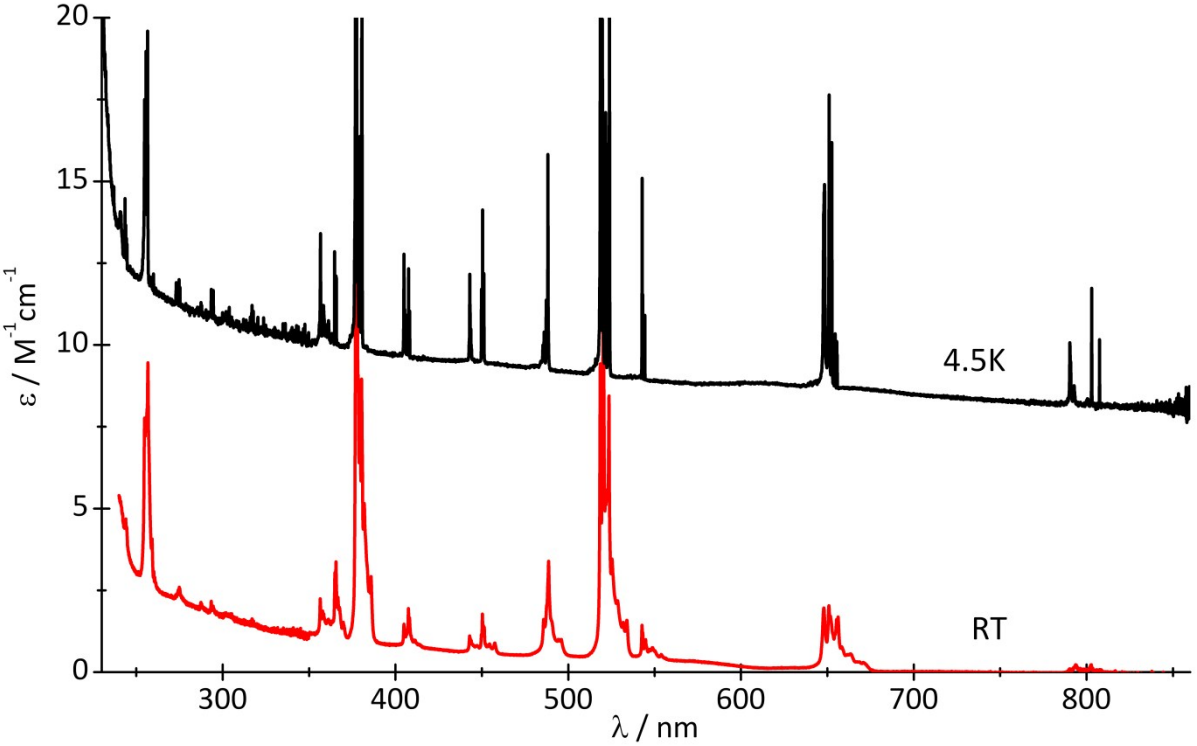

Figure S1. The UV-vis NIR spectra of I at RT and 4.2 K.

Table S4. The calculated and experimental concentrations (in M) of the species existing in solutions of Er(III)-EDTA-carbonate system (where [ML] = [Er(EDTA)$(H_2O)_2$], [MLA] = [Er(EDTA)(CO_3)], [MLOH] = [Er(EDTA)(OH)$(H_2O)_2$])

pH	A_{tot}	ML_{tot}	$[ML]_{calc}$	$[ML]_{exp}$	$[MLA]_{calc}$	$[MLA]_{exp}$	$[MLOH]_{calc}$	$[MLOH]_{exp}$	[A]
6.98	6.853E-03	2.980E-02	2.85E-02	2.78E-02	1.32E-03	1.63E-03	0	0	1.06E-05
6.87	1.367E-02	2.971E-02	2.77E-02	2.70E-02	2.04E-03	2.49E-03	0	0	1.68E-05
6.86	2.045E-02	2.963E-02	2.67E-02	2.58E-02	2.90E-03	3.52E-03	0	0	2.47E-05
6.89	2.719E-02	2.955E-02	2.56E-02	2.46E-02	3.97E-03	4.57E-03	0	0	3.53E-05
6.91	3.389E-02	2.947E-02	2.45E-02	2.35E-02	4.98E-03	5.65E-03	0	0	4.63E-05
6.94	4.056E-02	2.939E-02	2.33E-02	2.23E-02	6.10E-03	6.73E-03	0	0	5.97E-05
6.97	4.719E-02	2.931E-02	2.21E-02	2.12E-02	7.23E-03	7.60E-03	0	0	7.47E-05
7.04	5.378E-02	2.923E-02	2.03E-02	1.98E-02	8.92E-03	9.09E-03	0	0	1.00E-04
7.07	6.034E-02	2.915E-02	1.90E-02	1.85E-02	1.01E-02	1.02E-02	0	0	1.21E-04
7.12	6.687E-02	2.907E-02	1.75E-02	1.72E-02	1.16E-02	1.14E-02	0	0	1.51E-04
7.14	7.336E-02	2.899E-02	1.64E-02	1.61E-02	1.26E-02	1.24E-02	0	0	1.74E-04
7.19	7.981E-02	2.892E-02	1.49E-02	1.48E-02	1.40E-02	1.37E-02	0	0	2.13E-04
7.24	9.261E-02	2.876E-02	1.29E-02	1.30E-02	1.59E-02	1.53E-02	0	0	2.81E-04
7.29	1.053E-01	2.861E-02	1.10E-02	1.16E-02	1.76E-02	1.65E-02	0	0	3.62E-04
7.34	1.178E-01	2.846E-02	9.43E-03	9.95E-03	1.90E-02	1.80E-02	0	0	4.60E-04
7.41	1.302E-01	2.831E-02	7.75E-03	8.38E-03	2.05E-02	1.93E-02	0	0	6.04E-04
7.47	1.425E-01	2.816E-02	6.45E-03	7.25E-03	2.17E-02	2.04E-02	0	0	7.67E-04
7.52	1.546E-01	2.801E-02	5.45E-03	6.23E-03	2.26E-02	2.13E-02	0	0	9.44E-04
7.58	1.785E-01	2.772E-02	4.20E-03	4.61E-03	2.35E-02	2.24E-02	0	0	1.28E-03
7.68	2.020E-01	2.744E-02	3.01E-03	3.64E-03	2.44E-02	2.31E-02	0	0	1.85E-03
7.76	2.474E-01	2.689E-02	2.03E-03	2.25E-03	2.49E-02	2.39E-02	0	0	2.79E-03
7.89	2.911E-01	2.636E-02	1.27E-03	1.35E-03	2.51E-02	2.43E-02	0	0	4.50E-03
7.99	3.734E-01	2.537E-02	7.56E-04	6.44E-04	2.46E-02	2.40E-02	0	0	7.41E-03
10.00	6.947E-03	2.980E-02	1.90E-02	2.01E-02	6.83E-03	7.85E-03	3.94E-03	2.27E-03	8.18E-05
9.11	1.389E-02	2.971E-02	1.62E-02	1.65E-02	1.31E-02	1.38E-02	4.33E-04	0.00E+00	1.84E-04
8.77	1.667E-02	2.968E-02	1.48E-02	1.48E-02	1.47E-02	1.54E-02	1.80E-04	8.14E-06	2.27E-04
8.56	2.112E-02	2.963E-02	1.25E-02	1.25E-02	1.70E-02	1.75E-02	9.42E-05	2.74E-04	3.09E-04
8.49	2.557E-02	2.958E-02	1.04E-02	1.04E-02	1.91E-02	1.95E-02	6.66E-05	2.70E-04	4.18E-04
8.49	3.001E-02	2.953E-02	8.36E-03	8.27E-03	2.11E-02	2.15E-02	5.35E-05	2.12E-04	5.76E-04
8.55	3.446E-02	2.947E-02	6.31E-03	6.35E-03	2.31E-02	2.33E-02	4.64E-05	9.55E-05	8.35E-04
8.64	3.891E-02	2.942E-02	4.52E-03	4.66E-03	2.49E-02	2.50E-02	4.09E-05	2.34E-04	1.25E-03
8.84	4.446E-02	2.936E-02	2.56E-03	2.33E-03	2.68E-02	2.69E-02	3.67E-05	0.00E+00	2.38E-03
9.13	5.558E-02	2.923E-02	1.01E-03	6.82E-04	2.82E-02	2.84E-02	2.82E-05	5.88E-05	6.37E-03
9.32	6.947E-02	2.907E-02	4.98E-04	2.44E-04	2.86E-02	2.86E-02	2.15E-05	8.87E-05	1.31E-02
9.50	0	2.953E-02	2.77E-02	2.77E-02	0	0	1.82E-03	7.07E-04	0
9.73	0	2.949E-02	2.65E-02	2.67E-02	0	0	2.95E-03	1.58E-03	0
9.87	0	2.946E-02	2.55E-02	2.59E-02	0	0	3.92E-03	2.51E-03	0
9.97	0	2.943E-02	2.47E-02	2.49E-02	0	0	4.77E-03	3.26E-03	0
10.05	0	2.940E-02	2.39E-02	2.39E-02	0	0	5.54E-03	4.26E-03	0
10.16	0	2.935E-02	2.26E-02	2.24E-02	0	0	6.76E-03	5.77E-03	0
10.28	0	2.928E-02	2.10E-02	2.04E-02	0	0	8.29E-03	7.42E-03	0
10.43	0	2.919E-02	1.87E-02	1.76E-02	0	0	1.04E-02	1.03E-02	0
10.59	0	2.909E-02	1.61E-02	1.49E-02	0	0	1.30E-02	1.30E-02	0
10.74	0	2.900E-02	1.36E-02	1.22E-02	0	0	1.54E-02	1.59E-02	0
10.89	0	2.890E-02	1.11E-02	9.55E-03	0	0	1.78E-02	1.85E-02	0
11.11	0	2.879E-02	7.85E-03	6.64E-03	0	0	2.09E-02	2.15E-02	0
11.33	0	2.870E-02	5.29E-03	4.34E-03	0	0	2.34E-02	2.36E-02	0
11.58	0	2.861E-02	3.22E-03	2.58E-03	0	0	2.54E-02	2.55E-02	0
11.81	0	2.852E-02	1.98E-03	1.47E-03	0	0	2.65E-02	2.64E-02	0
12.66	2.551E-02	2.906E-02	0	0	1.14E-02	1.04E-02	1.75E-02	1.82E-02	1.41E-02
12.67	2.832E-02	2.900E-02	0	0	1.22E-02	1.12E-02	1.67E-02	1.74E-02	1.61E-02
12.68	3.111E-02	2.890E-02	0	0	1.28E-02	1.20E-02	1.59E-02	1.64E-02	1.83E-02
12.69	3.391E-02	2.878E-02	0	0	1.34E-02	1.27E-02	1.52E-02	1.56E-02	2.04E-02
12.71	3.669E-02	2.869E-02	0	0	1.39E-02	1.34E-02	1.47E-02	1.48E-02	2.28E-02
12.72	3.947E-02	2.853E-02	0	0	1.43E-02	1.39E-02	1.41E-02	1.42E-02	2.51E-02
12.73	4.224E-02	2.838E-02	0	0	1.47E-02	1.44E-02	1.36E-02	1.35E-02	2.75E-02
12.74	4.570E-02	2.808E-02	0	0	1.51E-02	1.50E-02	1.28E-02	1.26E-02	3.05E-02
12.75	4.915E-02	2.779E-02	0	0	1.55E-02	1.55E-02	1.22E-02	1.17E-02	3.36E-02
12.76	5.327E-02	2.722E-02	0	0	1.57E-02	1.59E-02	1.14E-02	1.06E-02	3.75E-02
12.77	5.875E-02	2.668E-02	0	0	1.61E-02	1.65E-02	1.05E-02	9.69E-03	4.26E-02
12.78	6.421E-02	2.668E-02	0	0	1.66E-02	1.71E-02	9.96E-03	9.09E-03	4.75E-02
12.80	7.235E-02	2.668E-02	0	0	1.73E-02	1.81E-02	9.34E-03	8.10E-03	5.50E-02
12.82	8.312E-02	2.668E-02	0	0	1.80E-02	1.94E-02	8.62E-03	6.79E-03	6.51E-02
12.83	9.646E-02	2.668E-02	0	0	1.89E-02	2.04E-02	7.76E-03	5.82E-03	7.75E-02
12.83	1.097E-01	2.668E-02	0	0	1.97E-02	2.23E-02	6.97E-03	3.99E-03	8.99E-02

For calculations of species concentrations the following equations have been used:

$$\beta_{OH} = \frac{[MLOH]}{[ML] \cdot [OH]} \qquad (1)$$

$$\beta_{(A)} = \frac{[MLA]}{[ML] \cdot [A]} \qquad (2)$$

$$\beta_{(B)} = \frac{[MLA] \cdot [OH]}{[MLOH] \cdot [A]} \qquad (3)$$

For carbonic acid H_2CO_3 the following protonation constants were defined:

$$K_1 = \frac{[HA]}{[H] \cdot [A]} \qquad (4)$$

$$K_2 = \frac{[H_2A]}{[H]^2 \cdot [A]} \qquad (5)$$

$K_W = [H]\cdot[OH]$ (6)

where M = Er; L = EDTA, A = CO_3^{2-}

$ML_{tot} = [ML] + [MLOH] + [MLA]$ (7)

$A_{tot} = [A] + [MLA] + [HA] + [H_2A]$ (8)

Combination of dependences 1 - 8 gives the quadratic equation (9):

$$[ML]^2\cdot\{\beta_2 + \beta_1\beta_2[OH]\} + [ML]\cdot\{-\beta_2ML_{tot} + 1 + K_1[H] + K_2[H]^2 + \beta_1[OH] + \beta_1K_1K_W + \beta_1K_2K_W[H] + \beta_2A_{tot}\} - ML_{tot} - K_1[H]ML_{tot} - K_2[H]^2ML_{tot} = 0 \qquad (9)$$

The solution of equation 9 is as follow:

$$[ML]_{calc} = (-\{-\beta_2ML_{tot} + 1 + K_1[H] + K_2[H]^2 + \beta_1[OH] + \beta_1K_1K_W + \beta_1K_2K_W[H] + \beta_2A_{tot}\} + (\{-\beta_2ML_{tot} + 1 + K_1[H] + K_2[H]^2 + \beta_1[OH] + \beta_1K_1K_W + \beta_1K_2K_W[H] + \beta_2A_{tot}\}^2 - 4\cdot\{\beta_2 + \beta_1\beta_2[OH]\}\cdot\{- ML_{tot} - K_1[H]ML_{tot} - K_2[H]^2ML_{tot}\})^{1/2})/(2\cdot\{\beta_2 + \beta_1\beta_2[OH]\}) \qquad (10)$$

The $[ML]_{calc}$ values were calculated by minimizing the sum (11)

$$\sum([ML]_{calc}-[ML]_{exp})^2 \qquad (11)$$

where $[ML]_{exp}$ is experimental values of [ML] complex concentration.

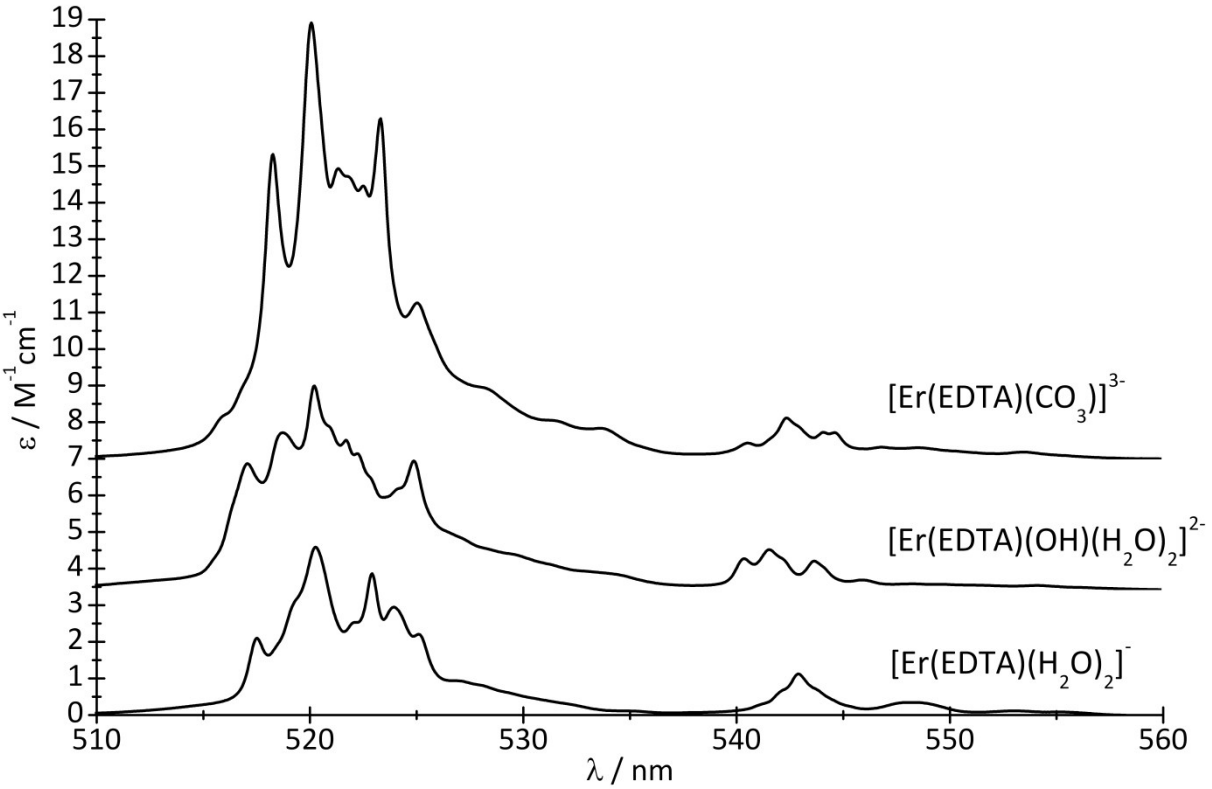

Figure S2. The $^4I_{15/2} \rightarrow {}^2H_{11/2}$ and $^4I_{15/2} \rightarrow {}^4S_{3/2}$ spectra of pure aqueous species: $[Er(EDTA)(H_2O)_2]^-$, $[Er(EDTA)(OH)(H_2O)_2]^{2-}$ and $[Er(EDTA)(H_2O)_2]^{3-}$ derived from the factor analysis[10] used for quantitative analysis of solutions.

Table S5. Experimental data taken for calculations of energy bonding ΔE

Complex		Bond lengths $\cdot 10^{10}$ [m]	z_+	z_-	E [J·mol^{-1}]	ΣE [J·mol^{-1}]
$[Er(EDTA)(H_2O)_2]^-$	Er-OH_2	2.3445	3	0	-4040	-8080
	Er-OH_2	2.3444	3	0	-4040	
$[Er(EDTA)(OH)(H_2O)_2]^{2-}$	Er-OH_2	2.5010	3	0	-3550	-30120
	Er-OH_2	2.4260	3	0	-3770	
	Er-OH	2.3293	3	-1	-22800	
$[Er(EDTA)(CO_3)]^{3-}$	Er-O(CO_3^{2-})	2.3300	3	$-\frac{2}{3}$	-15200	-30400
	Er-O(CO_3^{2-})	2.3280	3	$-\frac{2}{3}$	-15200	
$[Th(EDTA)(H_2O)_4]$	Th-OH_2	2.4910	4	0	-4770	-18480
	Th-OH_2	2.5230	4	0	-4650	
	Th-OH_2	2.5690	4	0	-4490	
	Th-OH_2	2.5460	4	0	-4570	
$[Th(EDTA)(CO_3)(H_2O)_2]^{2-}$	Th-OH_2	2.5323	4	0	-4620	-47640
	Th-OH_2	2.5323	4	0	-4620	
	Th-O(CO_3^{2-})	2.4538	4	$-\frac{2}{3}$	-19200	
	Th-O(CO_3^{2-})	2.4538	4	$-\frac{2}{3}$	-19200	
$[Th(EDTA)(CO_3)_2]^{4-}$	Th-O(CO_3^{2-})	2.4390	4	$-\frac{2}{3}$	-19300	-76900
	Th-O(CO_3^{2-})	2.4840	4	$-\frac{2}{3}$	-19000	
	Th-O(CO_3^{2-})	2.4310	4	$-\frac{2}{3}$	-19400	
	Th-O(CO_3^{2-})	2.4610	4	$-\frac{2}{3}$	-19200	

$\mu_{H2O} = 6.7 \cdot 10^{-30}$ [C·m^{-1}]
$\varepsilon_0 = 8.854 \cdot 10^{-12}$ [F·m^{-1}]
$\varepsilon = 78.7$
$\theta = 0^o$
$e = 1.602 \cdot 10^{-12}$ [C]
$N_A = 6.022 \cdot 10^{23}$ [mol^{-1}]

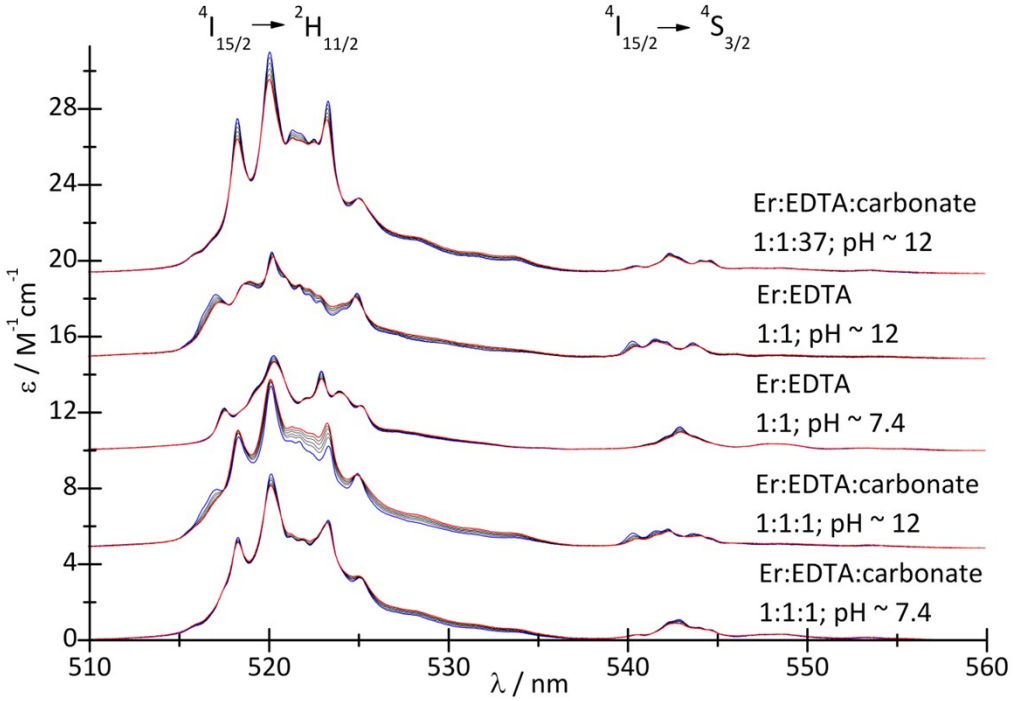

Figure S3. Absorption spectra of Er-EDTA-carbonate systems at different temperatures and pH. The spectra at low temperature (283K) are marked in blue. The highest temperature spectra (333K) are marked in red.

Determination of ΔG, ΔH and ΔS values of the of $[Er(EDTA)(CO_3)]^{3-}$ complex formation

To study the temperature influence on spectral change of hypersensitive f-f transitions two effects should be taken into consideration: chemical reactions that occur in solution and / or physical effects connected with the changes of Boltzmann distribution of crystal field levels of electronic ground state and broadening of spectra lines due to dynamics effects. The latter physical effect may complicate the analysis of chemical reactions in solution seriously. The spectra of the $^4I_{15/2} \rightarrow {}^2H_{11/2}$ and $^4I_{15/2} \rightarrow {}^4S_{3/2}$ transitions have been measured of the following solutions at temperatures:
(A) Er-EDTA 1:1 system at pH 7.4 as a model of $[Er(EDTA)(H_2O)_2]^-$ species;
(B) Er-EDTA 1:1 system at pH 12.6 as a model of $[Er(EDTA)(OH)(H_2O)_2]^{3-}$ species;
(C) Er-EDTA-carbonate 1:1:37 at pH 12.6 as a model of $[Er(EDTA)(CO_3)]^{3-}$ species.
Due to low thermal stability of bicarbonates the reactions (1) and (2)

$$[Er(EDTA)(H_2O)_2]^- + CO_3^{2-} \rightleftarrows [Er(EDTA)(CO_3)]^{3-} + 2H_2O \quad (1)$$

$$[Er(EDTA)(OH)(H_2O)_2]^- + CO_3^{2-} \rightleftarrows [Er(EDTA)(CO_3)]^{3-} + OH^- + 2H_2O \quad (2)$$

were studied in the temperature range between 283 and 333 K. The spectra of all these systems are presented in **Figure S3**. The weighted sum of the spectra of (A) and (C) was used to reproduce the spectra of the Er-EDTA-carbonate 1:1:1 systems at pH ~7.4 at the given temperature and consequently to obtain the molar fractions of Er(III) species in reaction (1). In the same way the molar fractions of Er(III) equlibrium species in reaction (2) at pH ~12.6 were determined combining the spectra of (B) and (C) with the spectra Er-EDTA-carbonate 1:1:1 systems at pH~12.6.
Because the pH of solutions under study depend on the temperature the combined glass electrode with built in temperature sensor has been used for these measurements. The glass electrode has been calibrated at a given temperature using three secondary pH-standard solutions according to UPAC recommendations[11] and procedures described in ref. [12].

Table S6. Empirical parameters used for pK_1 and pK_2 calculations of carbonic acid[35] at μ_{KCl} = 3.5 M (4.0 $mol \cdot kg^{-1}$) and pK_w for H_2O at different temperatures[28]

m	A_1	B_1	C_1	T	pK_1^*	pK_1
4.0	72.2986	-3166.18	-10.8732	281	6.48	6.21
4.0	72.2986	-3166.18	-10.8732	293	6.38	6.12
4.0	72.2986	-3166.18	-10.8732	303	6.33	6.05
4.0	72.2986	-3166.18	-10.8732	313	6.30	6.01
4.0	72.2986	-3166.18	-10.8732	323	6.29	5.97
4.0	72.2986	-3166.18	-10.8732	333	6.29	5.94
m	A_2	B_2	C_2	T	pK_2^*	pK_2
4.0	79.604	-3476.32	-12.0692	281	10.52	9.71
4.0	79.604	-3476.32	-12.0692	293	10.37	9.57
4.0	79.604	-3476.32	-12.0692	303	10.30	9.47
4.0	79.604	-3476.32	-12.0692	313	10.23	9.38
4.0	79.604	-3476.32	-12.0692	323	10.18	9.30
4.0	79.604	-3476.32	-12.0692	333	10.15	9.22

The pK_1 and pK_2 values were calculated using the empirical equations taken from ref.[13]

$pK_i^* - pK_i = A_i + B_i/T + C_i \ln T$

$A_1 = 35.2911m^{0.5} + 0.8491m - 0.32m^{1.5} + 0.055m^2$

$B_1 = -1583.09m^{0.5}$

$C_1 = -5.4366m^{0.5}$

$A_2 = 38.2746m^{0.5} + 1.6057m - 0.647m^{1.5} + 0.113m^2$

$B_2 = -1738.16m^{0.5}$

$C_2 = -6.0346m^{0.5}$

where pK_i^* and are the values for solutions at zero ionic strengths at a given temperature (T). pK_i are the values for solutions at molality (m) at a given temperature. The results of calculations are presented in Table S5.

Table S7. Experimental values of quantities determined from UV-vis measurements of Er(III)-EDTA-carbonate solutions at different temperatures used to calculate the ΔG, ΔH and ΔS values of $[Er(EDTA)(CO_3)]^{3-}$ complex formation (where [ML] = $[Er(EDTA)(H_2O)_2]$, [MLA] = $[Er(EDTA)(CO_3)]$, [MLOH] = $[Er(EDTA)(OH)(H_2O)_2]$)

T/K	A_{tot}/M	M_{tot}/M	[ML]/M	[MLA] /M	pH	pK_1	pK_2	pK_w	ΔG / J·mol^{-1}
281.9	0.05262	0.05263	0.02249	0.03014	7.76	9.69	15.89	14.69	-2.01E+04
294.5	0.05262	0.05263	0.02226	0.03037	7.63	9.55	15.66	14.20	-2.10E+04
303.5	0.05262	0.05263	0.02151	0.03112	7.60	9.46	15.52	13.90	-2.15E+04
312.9	0.05262	0.05263	0.02124	0.03139	7.53	9.38	15.38	13.56	-2.22E+04
322.5	0.05262	0.05263	0.02059	0.03204	7.52	9.30	15.26	13.24	-2.27E+04
331.2	0.05262	0.05263	0.02003	0.03260	7.51	9.23	15.16	12.98	-2.31E+04
T/K	A_{tot}/M	M_{tot}/M	[MLOH] /M	[MLA] /M	pH	pK_1	pK_2	pK_w	ΔG/ J·mol^{-1}
280.9	0.05156	0.05156	0.03030	0.02126	12.95	9.70	15.89	14.69	1.98E+03
294.0	0.05156	0.05156	0.02664	0.02491	12.50	9.56	15.66	14.20	8.54E+02
302.5	0.05156	0.05156	0.02486	0.02670	12.20	9.47	15.52	13.90	3.51E+02
312.8	0.05156	0.05156	0.02251	0.02905	12.04	9.38	15.38	13.56	-1.42E+03
323.4	0.05156	0.05156	0.02058	0.03098	11.62	9.29	15.26	13.24	-1.55E+03
332.5	0.05156	0.05156	0.01873	0.03283	11.40	9.22	15.16	12.98	-2.52E+03

References

1 R. Janicki, A. Mondry, *Phys. Chem. Chem. Phys*., 2014, **16** 26823–26831.
2 B. R. Judd, *Phys. Rev*., 1962, **127**, 750–761.
3 G. S. Ofelt, *J. Chem. Phys*., 1962, **37**, 511–519.
4 a) S. F. Mason, G. E. Tranter, *Chem. Phys. Lett*., 1983, **94**, 29–33; b) S. F. Mason, *Inorg. Chim. Acta*, 1984, **94**, 313–322; c) R. D. Peacock, *Struct. Bonding* ,Berlin, 1975, **22**, 83–219; d) S. F. Mason, *Struct. Bonding*, Berlin, 1980, **39**, 43–79; e) A. Mondry, P. Starynowicz, *J. Alloys Compd*., 1995, **225**, 367–371.
5 a) C. K. Jørgensen, R. Reisfeld, *J. Less. Comm . Met.*, 1983, **93**, 107-112; b) D. E. Henrie, G. R. Choppin, *J. Chem. Phys*., 1968, **49**, 477–481; c) D. E. Henrie, *Mol. Phys*. 1974, **28**, 415–421; d) Y. M. Poon, D. J. Newman, *J. Phys. C: Solid State Phys*. 1984, **17**, 4319–4325; e) M. Atanasov, C. Daul, H. U. Güdel, T. A. Wesołowski, M. Zbiri, *Inorg. Chem.*, 2005, **44**, 2954–2963; f) L. Petit, A. Borel, C. Daul, P. Maldivi, C. Adamo, *Inorg. Chem*., 2006, **45**, 7382–7388.
6 a) C. K. Jørgensen, B. R. Judd, *Mol. Phys*., 1964, **8**, 281–290; b) D. M. Gruen, C. W. DeKock, *J. Chem. Phys*., 1966, **45**, 455–460.
7 a) S. F. Mason, *Inorg. Chim. Acta*, 1984, **94**, 313–322; b) C. Görller-Walrand, K. Binnemans in Handbook on the Physics and Chemistry of Rare Earths ,Eds.: K. A. Gschneidner, Jr., L. Eyring), Elsevier, 1998, **25**, 101–264; c) R. Janicki, P. Starynowicz, A. Mondry, *Eur. J. Inorg. Chem.,* 2011, 3601–3616
8 C. K. Jørgensen, R. Reisfeld, *J. Less. Comm . Met.*, 1983, **93**, 107-112.
9 a) J. W. Rohleder, *Ann. Soc. Chim. Polonorum,* 1972, **46**, 2089–2097; b) B. W. N. Lo, *J. Phys. Chem. Solids* 1973, **34**, 513–520.
10 A. Rossberg, T. Reich and G. Bernhard, *Anal. Bioanal. Chem*., 2003, **376**, 631.
11 R. P. Buck, S. Rondinini, A. K. Covington, F. G. K. Baucke, C. M. A. Brett, M. F. Camões, M. J. T. Milton, T. Mussini, R. Naumann, K. W. Pratt, P. Spitzer, G. S. Wilson, *Pure Appl. Chem.*, 2002, **74**, 2169–2200.
12 B. Modrzejewski, *Pomiary pH*, Wydawnictwo Naukowo Techniczne, Warszawa 1971.
13 F. Millero, F. Huang, T. Graham, D. Pierrot, *Geochim. Cosm. Acta*, 2007, **71**, 46-55.