Electronic Supplementary Information

Mononuclear and polynuclear complexes ligated by an iminodiacetic acid derivative: synthesis, structure, solution studies and magnetic properties

Roberto Puentes,[a] Julia Torres,[a] Carlos Kremer,*[a] Joan Cano[b,c], Francesc Lloret[b], Davide Capucci[d], Alessia Bacchi[d]

[a] Cátedra de Química Inorgánica, Departamento Estrella Campos, Facultad de Química, Universidad de la República, Avda. General Flores 2124, Montevideo, Uruguay. E-mail: ckremer@fq.edu.uy
[b] Instituto de Ciencia Molecular, Universidad de Valencia, C/ Catedrático José Beltrán, 2. E-46980 Paterna (Valencia), Spain.
[c] Fundació General de la Universitat de València (FGUV)
[d] Dipartimento di Chimica, Università di Parma, Viale delle Scienze 17A, 43124 Parma, Italy

Table S1. Calculated spin configurations and their relative energies as a function of different J_i constants for model **Gd_4**. The spin configuration used as a reference is that with the maximum multiplicity that is generated from the parallel alignment of all local spin moments of the Gd(III) ions. Only the centers with an antiparallel (negative) alignment of their spin moment are noted.

Spin conf	S	J_a	J_b	J_c
{1,4}	0	56	0	56
{1,2}	0	0	28	56
{1,3}	0	56	28	0
{1}	7	28	0	28
{2}	7	28	28	28

Table S2. Hydrolysis constants of the Ln ions ($Ln^{3+} + H_2O \rightarrow [Ln(OH)]^{2+} + H^+$, $*K_1$) and protonation constants of bzlida determined at 25.0 °C in 0.50 mol L^{-1} Me_4NCl.

Protonation of bzlida		Hydrolysis of Ln		
Equilibrium	log K	Ln	log $*K_1$	σ
$L^{2-} + H^+ \rightarrow HL^-$	8.80(1)	Ce	-8.0(1)	0.3
$L^{2-} + 2\ H^+ \rightarrow H_2L$	11.27(3)	Sm	-7.3(1)	0.7
$L^{2-} + 3\ H^+ \rightarrow H_3L^+$	13.46(9)	Gd	-7.51(6)	0.1
σ	0.8	Yb	-7.4(4)	0.4

Table S3 Bond distances and angles in the metal coordination

Bond distances (Angstrom) with su's and angles (°) in the coordination sphere for $[Nd_2(bzlida)_3]\cdot 3H_2O$

Nd1 - N1 2.8564(4)	Nd1 - O5 2.5060(4)	Nd2 - N2 2.6841(1)
Nd1 - O1 2.5433(3)	Nd1 - O11 2.6120(3)	Nd2 - N3 2.7603(1)
Nd1 - O3 2.4343(4)	Nd1 - O14 2.4982(3)	Nd2 - O1 2.5142(1)

Nd2 - O5 2.4997(1)	O3 - Nd1 - O14 136.62	O1 - Nd2 - O7 135.01
Nd2 - O7 2.4390(1)	O5 - Nd1 - O11 62.71	O1 - Nd2 - O9 142.91
Nd2 - O9 2.4238(1)	O5 - Nd1 - O14 78.97	O1 - Nd2 - O11 65.48
Nd2 - O11 2.5388(1)	O11 - Nd1 - O14 124.18	O1 - Nd2 - O13 80.00
Nd2 - O13 2.4798(1)	N2 - Nd2 - N3 123.12	O1 - Nd2 - O15 69.00
Nd2 - O15 2.5096(1)	N2 - Nd2 - O1 134.58	O5 - Nd2 - O7 104.72
Nd1 ...O3 2.4902(4)-x+1,-y+1,-z	N2 - Nd2 - O5 63.73	O5 - Nd2 - O9 132.32
Nd1 ..O8 2.4416(3) -x+3/2,+y+1/2,-z+1/2	N2 - Nd2 - O7 63.09	O5 - Nd2 - O11 63.85
Nd1 ...O12 2.4626 (3) -x+1,-y+1,-z	N2 - Nd2 - O9 74.63	O5 - Nd2 - O13 141.59
N1 - Nd1 - O1 60.22	N2 - Nd2 - O11 91.70	O5 - Nd2 - O15 72.01
N1 - Nd1 - O3 63.80	N2 - Nd2 - O13 140.37	O7 - Nd2 - O9 73.70
N1 - Nd1 - O5 125.77	N2 - Nd2 - O15 98.14	O7 - Nd2 - O11 154.46
N1 - Nd1 - O11 109.34	N3 - Nd2 - O1 81.35	O7 - Nd2 - O13 78.59
N1 - Nd1 - O14 126.12	N3 - Nd2 - O5 125.00	O7 - Nd2 - O15 67.32
O1 - Nd1 - O3 84.63	N3 - Nd2 - O7 127.68	O9 - Nd2 - O11 96.77
O1 - Nd1 - O5 70.34	N3 - Nd2 - O9 61.68	O9 - Nd2 - O13 85.79
O1 - Nd1 - O11 64.01	N3 - Nd2 - O11 61.53	O9 - Nd2 - O15 138.90
O1 - Nd1 - O14 138.54	N3 - Nd2 - O13 72.55	O11 - Nd2 - O13 125.11
O3 - Nd1 - O5 133.64	N3 - Nd2 - O15 138.71	O11 - Nd2 - O15 124.13
O3 - Nd1 - O11 71.38	O1 - Nd2 - O5 70.92	O13 - Nd2 - O15 74.47

Bond distances (Angstrom) with su's and angles (°) in the coordination sphere for $[Sm_2(bzlida)_3]\cdot 3H_2O$

Sm1 - N1 2.8247(4)	O1 - Sm1 - O3 85.40	N3 - Sm2 - O15 138.56
Sm1 - O1 2.5167(3)	O1 - Sm1 - O5 70.30	O1 - Sm2 - O5 70.70
Sm1 - O3 2.4130(4)	O1 - Sm1 - O11 63.97	O1 - Sm2 - O7 134.31
Sm1 - O5 2.4801(4)	O1 - Sm1 - O14 138.69	O1 - Sm2 - O9 143.19
Sm1 - O11 2.5933(3)	O3 - Sm1 - O5 133.92	O1 - Sm2 - O11 65.60
Sm1 - O14 2.4718(3)	O3 - Sm1 - O11 71.85	O1 - Sm2 - O13 80.28
Sm2 - N2 2.6585(1)	O3 - Sm1 - O14 135.74 1	O1 - Sm2 - O15 68.60
Sm2 - N3 2.7434(1)	O5 - Sm1 - O11 62.42	O5 - Sm2 - O7 105.33
Sm2 - O1 2.4903(1)	O5 - Sm1 - O14 78.94	O5 - Sm2 - O9 132.82
Sm2 - O5 2.4819(1)	O11 - Sm1 - O14 123.751	O5 - Sm2 - O11 63.63
Sm2 - O7 2.4242(1)	N2 - Sm2 - N3 123.57	O5 - Sm2 - O13 141.65
Sm2 - O9 2.3975(1)	N2 - Sm2 - O1 134.89	O5 - Sm2 - O15 71.36
Sm2 - O11 2.5077(1)	N2 - Sm2 - O5 64.22	O7 - Sm2 - O9 73.49
Sm2 - O13 2.4431(1)	N2 - Sm2 - O7 63.55	O7 - Sm2 - O11 155.22
Sm2 - O15 2.4905(1)	N2 - Sm2 - O9 74.55	O7 - Sm2 - O13 77.51
Sm1 ...O3 2.4709 (4)-x+1,-y+1,-z	N2 - Sm2 - O11 91.96	O7 - Sm2 - O15 67.32
Sm1 .O8 2.4161 (3) -x+3/2,+y+1/2,-z+1/2	N2 - Sm2 - O13 139.67	O9 - Sm2 - O11 97.36
Sm1 ...O12 2.4313 (3)-x+1,-y+1,-z	N2 - Sm2 - O15 97.86	O9 - Sm2 - O13 85.18
	N3 - Sm2 - O1 81.19	O9 - Sm2 - O15 138.93
N1 - Sm1 - O1 60.83	N3 - Sm2 - O5 124.98	O11 - Sm2 - O13 125.48
N1 - Sm1 - O3 64.53	N3 - Sm2 - O7 127.47	O11 - Sm2 - O15 123.48
N1 - Sm1 - O5 126.14	N3 - Sm2 - O9 62.16	O13 - Sm2 - O15 75.05
N1 - Sm1 - O11 110.14	N3 - Sm2 - O11 61.81	
N1 - Sm1 - O14 125.77	N3 - Sm2 - O13 72.35	

Bond distances (Angstrom) with su's and angles (°) in the coordination sphere for $[Eu_2(bzlida)_3]\cdot 3H_2O$

Eu1 - N1 2.8091(4)		O3 - Eu1 - O14 135.32
Eu1 - O1 2.5007(3)	Eu2 - Eu1 - N1 99.64	O5 - Eu1 - O11 62.30
Eu1 - O3 2.3983(4)	Eu2 - Eu1 - O1 38.70	O5 - Eu1 - O14 78.77
Eu1 - O5 2.4659(4)	Eu2 - Eu1 - O3 100.30	O11 - Eu1 - O14 123.34
Eu1 - O11 2.5823(3)	Eu2 - Eu1 - O5 38.42	Eu1 - Eu2 - N2 98.33
Eu1 - O14 2.4578(3)	Eu2 - Eu1 - O11 39.51	Eu1 - Eu2 - N3 92.05
Eu2 - N2 2.6497(2)	Eu2 - Eu1 - O14 117.19	Eu1 - Eu2 - O1 39.13
Eu2 - N3 2.7377(1)	N1 - Eu1 - O1 61.02	Eu1 - Eu2 - O5 38.29
Eu2 - O1 2.4773(1)	N1 - Eu1 - O3 65.05	Eu1 - Eu2 - O7 140.60
Eu2 - O5 2.4730(2)	N1 - Eu1 - O5 126.22	Eu1 - Eu2 - O9 138.38
Eu2 - O7 2.4110(1)	N1 - Eu1 - O11 110.54	Eu1 - Eu2 - O11 41.14
Eu2 - O9 2.3870(2)	N1 - Eu1 - O14 125.77	Eu1 - Eu2 - O13 119.60
Eu2 - O11 2.4973(1)	O1 - Eu1 - O3 85.90	Eu1 - Eu2 - O15 82.24
Eu2 - O13 2.4146(1)	O1 - Eu1 - O5 70.28	N2 - Eu2 - N3 123.62
Eu2 - O15 2.4732(1)	O1 - Eu1 - O11 64.07	N2 - Eu2 - O1 134.98
Eu1 ...O3 2.4553(4)-x+1,-y+1,-z	O1 - Eu1 - O14 138.66	N2 - Eu2 - O5 64.47
Eu1 .O8 2.4016 (3)-x+3/2,+y+1/2,-z+1/2	O3 - Eu1 - O5 134.03	N2 - Eu2 - O7 63.85
Eu1 ...O12 2.4189 (3)-x+1,-y+1,-z	O3 - Eu1 - O11 72.04	N2 - Eu2 - O9 74.48

N2	- Eu2 - O11	91.94	O1	- Eu2 - O7	133.99	O7	- Eu2 - O11	155.52
N2	- Eu2 - O13	139.35	O1	- Eu2 - O9	143.24	O7	- Eu2 - O13	76.93
N2	- Eu2 - O15	97.74	O1	- Eu2 - O11	65.66	O7	- Eu2 - O15	67.09
N3	- Eu2 - O1	81.24	O1	- Eu2 - O13	80.50	O9	- Eu2 - O11	97.46
N3	- Eu2 - O5	125.00	O1	- Eu2 - O15	68.61	O9	- Eu2 - O13	84.99
N3	- Eu2 - O7	127.29	O5	- Eu2 - O7	105.65	O9	- Eu2 - O15	138.91
N3	- Eu2 - O9	62.16	O5	- Eu2 - O9	132.95	O11	- Eu2 - O13	125.79
N3	- Eu2 - O11	62.05	O5	- Eu2 - O11	63.43	O11	- Eu2 - O15	123.38
N3	- Eu2 - O13	72.31	O5	- Eu2 - O13	141.70	O13	- Eu2 - O15	75.21
N3	- Eu2 - O15	138.62	O5	- Eu2 - O15	71.23			
O1	- Eu2 - O5	70.55	O7	- Eu2 - O9	73.58			

Bond distances (Angstrom) with su's and angles (°) in the coordination sphere for $[Gd_2(bzlida)_3]\cdot 3H_2O$

Gd1	- N2 2.7968(2)		O2	- Gd1 - O3	72.25	N3	- Gd2 - O10	64.78
Gd1	- O2 2.5688(3)		O2	- Gd1 - O7	63.93	N3	- Gd2 - O13	64.09
Gd1	- O3 2.3993(2)		O2	- Gd1 - O10	62.28	O1	- Gd2 - O2	97.55
Gd1	- O7 2.4924(2)		O2	- Gd1 - O15	123.46	O1	- Gd2 - O4	85.35
Gd1	- O10 2.4555(2)		O3	- Gd1 - O7	86.25	O1	- Gd2 - O7	143.19
Gd1	- O15 2.4540(2)		O3	- Gd1 - O10	134.25	O1	- Gd2 - O9	138.97
Gd2	- N1 2.7350(2)		O3	- Gd1 - O15	134.90	O1	- Gd2 - O10	132.92
Gd2	- N3 2.6383(2)		O7	- Gd1 - O10	70.12	O1	- Gd2 - O13	73.80
Gd2	- O1 2.3783(2)		O7	- Gd1 - O15	138.72	O2	- Gd2 - O4	125.85
Gd2	- O2 2.4922(2)		O10	- Gd1 - O15	78.94	O2	- Gd2 - O7	65.52
Gd2	- O4 2.4006(2)		N1	- Gd2 - N3	123.58	O2	- Gd2 - O9	123.20
Gd2	- O7 2.4606(2)		N1	- Gd2 - O1	62.36	O2	- Gd2 - O10	63.32
Gd2	- O9 2.4700(2)		N1	- Gd2 - O2	62.00	O2	- Gd2 - O13	155.97
Gd2	- O10 2.4607(2)		N1	- Gd2 - O4	72.58	O4	- Gd2 - O7	80.28
Gd2	- O13 2.4029(2)		N1	- Gd2 - O7	80.99	O4	- Gd2 - O9	75.09
Gd1	...O3 2.4446 (4)	-x+1,-y+1,-z	N1	- Gd2 - O9	138.70	O4	- Gd2 - O10	141.38
Gd1	...O5 2.4061 (3)	-x+1,-y+1,-z	N1	- Gd2 - O10	124.82	O4	- Gd2 - O13	76.58
Gd1	...O8 2.3933 (4)	-x+3/2,+y-1/2,-z+1/2	N1	- Gd2 - O13	127.45	O7	- Gd2 - O9	68.74
N2	- Gd1 - O2	110.76	N3	- Gd2 - O1	74.17	O7	- Gd2 - O10	70.56
N2	- Gd1 - O3	65.14	N3	- Gd2 - O2	92.10	O7	- Gd2 - O13	133.69
N2	- Gd1 - O7	61.43	N3	- Gd2 - O4	139.22	O9	- Gd2 - O10	71.09
N2	- Gd1 - O10	126.40	N3	- Gd2 - O7	135.30	O9	- Gd2 - O13	66.79
N2	- Gd1 - O15	125.46	N3	- Gd2 - O9	97.70	O10	- Gd2 - O13	105.81

Bond distances (Angstrom) with su's and angles (°) in the coordination sphere for $[La(Hbzlida)(bzlida)]\cdot H_2O$

La	- N1 2.8800(4)		La	...O8 2.4148 (4)	x-1/2,-y+1/2,+z	O2	- La - O3	100.97
La	- O2 2.4654(3)		La	...O10 2.6158 (5)	x+1/2,-y+1/2,+z	O2	- La - O5	149.67
La	- O3 2.6189(3)					O2	- La - O9	72.17
La	- O5 2.5100(3)		N1	- La - O2	61.65	O3	- La - O5	73.25
La	- O9 2.6342(3)		N1	- La - O3	59.15	O3	- La - O9	132.07
La	...O3 2.6951 (3)	x+1/2,-y+1/2,+z	N1	- La - O5	129.82	O5	- La - O9	134.02
La	...O6 2.4632 (4)	x+1/2,-y+1/2,+z	N1	- La - O9	77.52			

Bond distances (Angstrom) with su's and angles (°)with su's in the coordination sphere for $[Cu(Hbzlida)_2]\cdot 4H_2O$

Cu1	- O2 2.426(1)		O2	- Cu1 - O3	95.34	0.02		
Cu1	- O3 1.9529(9)		O2	- Cu1 - N1	75.60	0.02		
Cu1	- N1 2.0236(9)		O3	- Cu1 - N1	86.16	0.02		

Bond distances (Angstrom) with su's and angles (°) with su's in the coordination sphere for $[Cu(bzlida)_2\{Er(AcO)(H_2O)_5\}_2]$ $[Cu(bzlida)_2]\cdot 6H_2O$

Er1	- O1 2.3339(9)		Cu1	- O7 1.9726(6)		O1	- Er1 - O9	114.64	0.03
Er1	- O9 2.4475(14)		Cu2	- N1 2.0444(8)		O1	- Er1 - O10	75.62	0.02
Er1	- O10 2.3819(10)		Cu2	- O2 2.3549(8)		O1	- Er1 - O11	74.72	0.03
Er1	- O11 2.3327(11)		Cu2	- O3 1.9951(7)		O1	- Er1 - O12	141.38	0.03
Er1	- O12 2.3274(9)		Cu1	...N2 2.0645 (7)	-x+1,-y+1,-z	O1	- Er1 - O13	141.08	0.04
Er1	- O13 2.3822(12)		Cu1	...O6 2.4730 (8)	-x+1,-y+1,-z	O1	- Er1 - O14	74.49	0.03
Er1	- O14 2.2878(10)		Cu1	...O7 1.9726 (6)	-x+1,-y+1,-z	O1	- Er1 - O15	82.26	0.02
Er1	- O15 2.3508(10)		Cu2	...N1 2.0444 (8)	-x+2,-y+1,-z	O9	- Er1 - O10	54.17	0.02
Er1	- C100 2.7924(11		Cu2	...O2 2.3549 (8)	-x+2,-y+1,-z	O9	- Er1 - O11	128.78	0.03
Cu1	- N2 2.0645(7)		Cu2	...O3 1.9951 (7)	-x+2,-y+1,-z	O9	- Er1 - O12	82.97	0.02
Cu1	- O6 2.4730(8)					O9	- Er1 - O13	75.12	0.02

O9	- Er1	- O14	78.27	0.03	O11	- Er1	- O13	71.13	0.03	O14	- Er1	- O15	88.03	0.03
O9	- Er1	- O15	153.79	0.03	O11	- Er1	- O14	145.82	0.04	N2	- Cu1	- O6	75.84	0.02
O10	- Er1	- O11	83.97	0.02	O11	- Er1	- O15	73.45	0.02	N2	- Cu1	- O7	85.70	0.02
O10	- Er1	- O12	135.65	0.03	O12	- Er1	- O13	74.86	0.03	O6	- Cu1	- O7	94.73	0.03
O10	- Er1	- O13	82.71	0.03	O12	- Er1	- O14	76.27	0.03	N1	- Cu2	- O2	74.85	0.02
O10	- Er1	- O14	102.33	0.03	O12	- Er1	- O15	72.04	0.02	N1	- Cu2	- O3	84.98	0.02
O10	- Er1	- O15	151.85	0.03	O13	- Er1	- O14	142.63	0.04	O2	- Cu2	- O3	93.65	0.03
O11	- Er1	- O12	122.20	0.03	O13	- Er1	- O15	104.91	0.03					

Table S4 Hydrogen bond geometry

(**) Values normalized following G.A.Jeffrey & L.Lewis, Carbohydr.Res.
(1978).60,179; R.Taylor, O.Kennard, Acta Cryst.(1983).B39,133.

Possible hydrogen bonds for Nd2(bzlida)3.3H2O

Donor-H	Donor...Acceptor		H...Acceptor		Donor-H.....Acceptor	
O13 -H13B	O13 ...O2	(0)	H13B ...O2	(0)	O13 -H13B ...O2	(0)
0.867(.000)	2.677(.000)		1.861(.000)		156.03(0.00)	
0.938			1.797		155.11	(**)
O14 -H14B	O14 ...O6	(0)	H14B ...O6	(0)	O14 -H14B ...O6	(0)
0.865(.000)	2.740(.000)		1.908(.000)		161.10(0.01)	
0.938			1.839		160.36	(**)
O15 -H15B	O15 ...O2	(0)	H15B ...O2	(0)	O15 -H15B ...O2	(0)
0.869(.000)	2.948(.000)		2.638(.000)		102.29(0.00)	
0.938			2.624		100.81	(**)
O15 -H15A	O15 ...O10	(1)	H15A ...O10	(1)	O15 -H15A ...O10	(1)
0.864(.000)	2.650(.000)		1.788(.000)		175.31(0.01)	
0.938			1.714		175.11	(**)
O14 -H14B	O14 ...O4	(2)	H14B ...O4	(2)	O14 -H14B ...O4	(2)
0.865(.000)	2.924(.000)		2.649(.000)		99.83(0.00)	
0.938			2.638		98.27	(**)
O14 -H14A	O14 ...O10	(5)	H14A ...O10	(5)	O14 -H14A ...O10	(5)
0.884(.000)	2.907(.000)		2.041(.000)		166.01(0.00)	
0.938			1.989		165.63	(**)
O13 -H13A	O13 ...O6	(6)	H13A ...O6	(6)	O13 -H13A ...O6	(6)
0.893(.000)	2.700(.000)		1.828(.000)		164.51(0.00)	
0.938			1.785		164.13	(**)

Equivalent positions:
(0) x,y,z
(1) -x+1/2+1,+y+1/2,-z+1/2
(2) -x+1,-y+1,-z
(5) x,+y+1,+z
(6) -x+1/2+1,+y-1/2,-z+1/2

Possible hydrogen bonds for Sm2(bzlida)3.3H2O

Donor-H	Donor...Acceptor		H...Acceptor		Donor-H.....Acceptor	
O13 -H13B	O13 ...O2	(0)	H13B ...O2	(0)	O13 -H13B ...O2	(0)
0.892(.000)	2.655(.000)		1.819(.000)		155.05(0.01)	
0.938			1.778		154.43	(**)
O14 -H14B	O14 ...O6	(0)	H14B ...O6	(0)	O14 -H14B ...O6	(0)
0.897(.000)	2.728(.000)		1.883(.000)		156.16(0.01)	
0.938			1.846		155.65	(**)
O15 -H15A	O15 ...O10	(1)	H15A ...O10	(1)	O15 -H15A ...O10	(1)
0.882(.000)	2.651(.000)		1.787(.000)		166.21(0.01)	
0.938			1.732		165.77	(**)
O14 -H14A	O14 ...O10	(5)	H14A ...O10	(5)	O14 -H14A ...O10	(5)
0.903(.000)	2.924(.000)		2.049(.000)		162.86(0.01)	
0.938			2.016		162.57	(**)
O13 -H13A	O13 ...O6	(6)	H13A ...O6	(6)	O13 -H13A ...O6	(6)
0.897(.000)	2.698(.000)		1.809(.000)		170.23(0.01)	
0.938			1.769		170.00	(**)

Equivalent positions:
(0) x,y,z
(1) -x+1/2+1,+y+1/2,-z+1/2
(5) x,+y+1,+z
(6) -x+1/2+1,+y-1/2,-z+1/2

Possible hydrogen bonds for Eu2(bzlida)3.3H2O

Donor-H	Donor...Acceptor		H...Acceptor		Donor-H.....Acceptor	
O13 -H13B	O13 ...O2	(0)	H13B ...O2	(0)	O13 -H13B ...O2	(0)
0.873(.000)	2.647(.000)		1.814(.000)		158.76(0.01)	
0.938			1.754		157.99	(**)
O14 -H14B	O14 ...O6	(0)	H14B ...O6	(0)	O14 -H14B ...O6	(0)
0.906(.000)	2.715(.000)		1.880(.000)		152.41(0.01)	
0.938			1.851		151.95	(**)
O15 -H15A	O15 ...O10	(1)	H15A ...O10	(1)	O15 -H15A ...O10	(1)
0.892(.000)	2.649(.000)		1.762(.000)		172.68(0.01)	
0.938			1.716		172.49	(**)
O14 -H14A	O14 ...O10	(5)	H14A ...O10	(5)	O14 -H14A ...O10	(5)
0.898(.000)	2.944(.000)		2.073(.000)		163.05(0.01)	
0.938			2.035		162.72	(**)
O13 -H13A	O13 ...O6	(6)	H13A ...O6	(6)	O13 -H13A ...O6	(6)
0.898(.000)	2.697(.000)		1.812(.000)		168.33(0.01)	
0.938			1.773		168.07	(**)

Equivalent positions:
(0) x,y,z
(1) -x+1/2+1,+y+1/2,-z+1/2
(5) x,+y+1,+z
(6) -x+1/2+1,+y-1/2,-z+1/2

Possible hydrogen bonds for Gd2(bzlida)3.3H2O

Donor-H	Donor...Acceptor		H...Acceptor		Donor-H.....Acceptor	
O15 -H15B	O15 ...O14	(0)	H15B ...O14	(0)	O15 -H15B ...O14	(0)
0.886(.000)	2.715(.000)		1.950(.000)		143.76(0.01)	
0.938			1.908		142.83	(**)
O4 -H4A	O4 ...O14	(1)	H4A ...O14	(1)	O4 -H4A ...O14	(1)
0.884(.000)	2.701(.000)		1.819(.000)		175.17(0.01)	
0.938			1.765		175.02	(**)
O15 -H15B	O15 ...O13	(2)	H15B ...O13	(2)	O15 -H15B ...O13	(2)
0.886(.000)	3.024(.000)		2.467(.000)		121.32(0.01)	
0.938			2.440		120.27	(**)
O9 -H9B	O9 ...O12	(2)	H9B ...O12	(2)	O9 -H9B ...O12	(2)
0.877(.000)	2.643(.000)		1.796(.000)		161.54(0.01)	
0.938			1.738		160.90	(**)
O15 -H15A	O15 ...O6	(3)	H15A ...O6	(3)	O15 -H15A ...O6	(3)
0.887(.000)	2.890(.000)		2.456(.000)		110.55(0.01)	
0.938			2.439		109.43	(**)

Equivalent positions:
(0) x,y,z
(1) -x+1/2+1,+y+1/2,-z+1/2
(2) -x+1/2+1,+y-1/2,-z+1/2
(3) -x+1,-y+1,-z

Possible hydrogen bonds for La(Hbzlida)(bzlida).H2O

Donor-H	Donor...Acceptor		H...Acceptor		Donor-H.....Acceptor	
O9 -H9A	O9 ...O1	(7)	H9A ...O1	(7)	O9 -H9A ...O1	(7)
0.778(.000)	2.692(.000)		1.931(.000)		165.98(0.01)	
0.938			1.776		164.72	(**)

Equivalent positions:
(7) x+1/2,-y-1/2,+z

Possible hydrogen bonds for Cu(Hbzlida)2.4H2O

Donor-H	Donor...Acceptor	H...Acceptor	Donor-H.....Acceptor

O1	-H1	O1	...O6	(0)	H1	...O6	(0)	O1 -H1 ...O6 (0)
0.820(.000)		2.796(.001)			2.343(.001)			115.52(0.03)
0.938					2.295			112.86 (**)
O5	-H5B	O5	...O2	(0)	H5B	...O2	(0)	O5 -H5B ...O2 (0)
0.976(.001)		2.760(.001)			2.289(.001)			108.57(0.03)
0.938					2.302			109.47 (**)
O6	-H6A	O6	...O1	(0)	H6A	...O1	(0)	O6 -H6A ...O1 (0)
0.922(.000)		2.796(.001)			2.276(.001)			115.25(0.03)
0.938					2.269			114.89 (**)
O6	-H6B	O6	...O1	(5)	H6B	...O1	(5)	O6 -H6B ...O1 (5)
0.930(.000)		2.756(.001)			1.930(.001)			146.91(0.04)
0.938					1.923			146.77 (**)
O5	-H5B	O5	...O3	(5)	H5B	...O3	(5)	O5 -H5B ...O3 (6)
0.976(.001)		2.854(.001)			2.624(.001)			93.46(0.03)
0.938					2.626			94.29 (**)

Equivalent positions:
(0) x,y,z
(5) x-1/2,+y,-z+1/2
(6) -x+3,-y+1,-z+1

Possible hydrogen bonds for [Cu(bzlida)2(Er(CH3COO)(H2O)5)2] [Cu(bzlida)2] 6H2O

Donor-H		Donor...Acceptor			H...Acceptor			Donor-H.....Acceptor
O14	-H14B	O14	...O2	(0)	H14B	...O2	(0)	O14 -H14B ...O2 (0)
0.979(.000)		2.585(.001)			1.784(.001)			136.70(0.05)
0.938					1.814			137.60 (**)
O15	-H15B	O15	...O5	(0)	H15B	...O5	(0)	O15 -H15B ...O5 (0)
1.083(.000)		2.936(.001)			2.174(.001)			125.27(0.04)
0.938					2.262			128.28 (**)
O16	-H16A	O16	...O18	(0)	H16A	...O18	(0)	O16 -H16A ...O18 (0)
0.981(.000)		2.889(.001)			2.021(.001)			146.31(0.05)
0.938					2.057			146.98 (**)
O16	-H16B	O16	...O10	(0)	H16B	...O10	(0)	O16 -H16B ...O10 (0)
0.984(.000)		2.835(.001)			1.988(.001)			142.82(0.04)
0.938					2.025			143.61 (**)
O17	-H17B	O17	...O4	(0)	H17B	...O4	(0)	O17 -H17B ...O4 (0)
0.977(.000)		2.841(.001)			1.896(.001)			161.85(0.04)
0.938					1.933			162.21 (**)
O11	-H11A	O11	...O9	(1)	H11A	...O9	(1)	O11 -H11A ...O9 (1)
0.969(.000)		2.740(.001)			2.025(.001)			128.97(0.04)
0.938					2.045			129.65 (**)
O13	-H13B	O13	...O7	(2)	H13B	...O7	(2)	O13 -H13B ...O7 (2)
0.960(.000)		2.908(.001)			1.980(.001)			161.81(0.05)
0.938					2.001			162.01 (**)
O11	-H11B	O11	...O8	(2)	H11B	...O8	(2)	O11 -H11B ...O8 (2)
0.967(.000)		2.800(.001)			1.878(.001)			158.31(0.05)
0.938					1.906			158.64 (**)
O18	-H18D	O18	...O8	(2)	H18D	...O8	(2)	O18 -H18D ...O8 (2)
1.009(.000)		3.004(.001)			2.023(.001)			163.59(0.04)
0.938					2.091			164.14 (**)
O12	-H12A	O12	...O5	(3)	H12A	...O5	(3)	O12 -H12A ...O5 (3)
0.967(.001)		2.548(.001)			1.705(.001)			143.55(0.05)
0.938					1.728			144.11 (**)
O13	-H13A	O13	...O6	(3)	H13A	...O6	(3)	O13 -H13A ...O6 (3)
0.969(.000)		2.775(.001)			2.109(.001)			124.42(0.04)
0.938					2.127			125.12 (**)

O14	-H14A		O14	...O3	(4)	H14A	...O3	(4)	O14	-H14A	...O3 (4)
0.971(.001)			2.846(.001)			2.172(.001)			125.36(0.04)		
0.938						2.191			126.07		(**)
O18	-H18C		O18	...O17	(7)	H18C	...O17	(7)	O18	-H18C	...O17 (7)
0.975(.000)			2.957(.001)			2.073(.001)			149.91(0.04)		
0.938						2.105			150.41		(**)
O17	-H17A		O17	...O18	(8)	H17A	...O18	(8)	O17	-H17A	...O18 (8)
1.054(.000)			2.957(.001)			2.062(.001)			141.10(0.04)		
0.938						2.153			143.03		(**)

Equivalent positions:

(0) x,y,z
(1) x,+y+1,+z
(2) -x+1,-y+1,-z
(3) x,+y-1,+z
(4) -x+2,-y,-z
(7) -x+2,+y+1/2,-z+1/2
(8) -x+2,+y-1/2,-z+1/2

Figure S1 Tetranuclear [**Gd_4** (a)] and dinuclear [**Gd_2** (b)] molecular models used in the theoretical study.

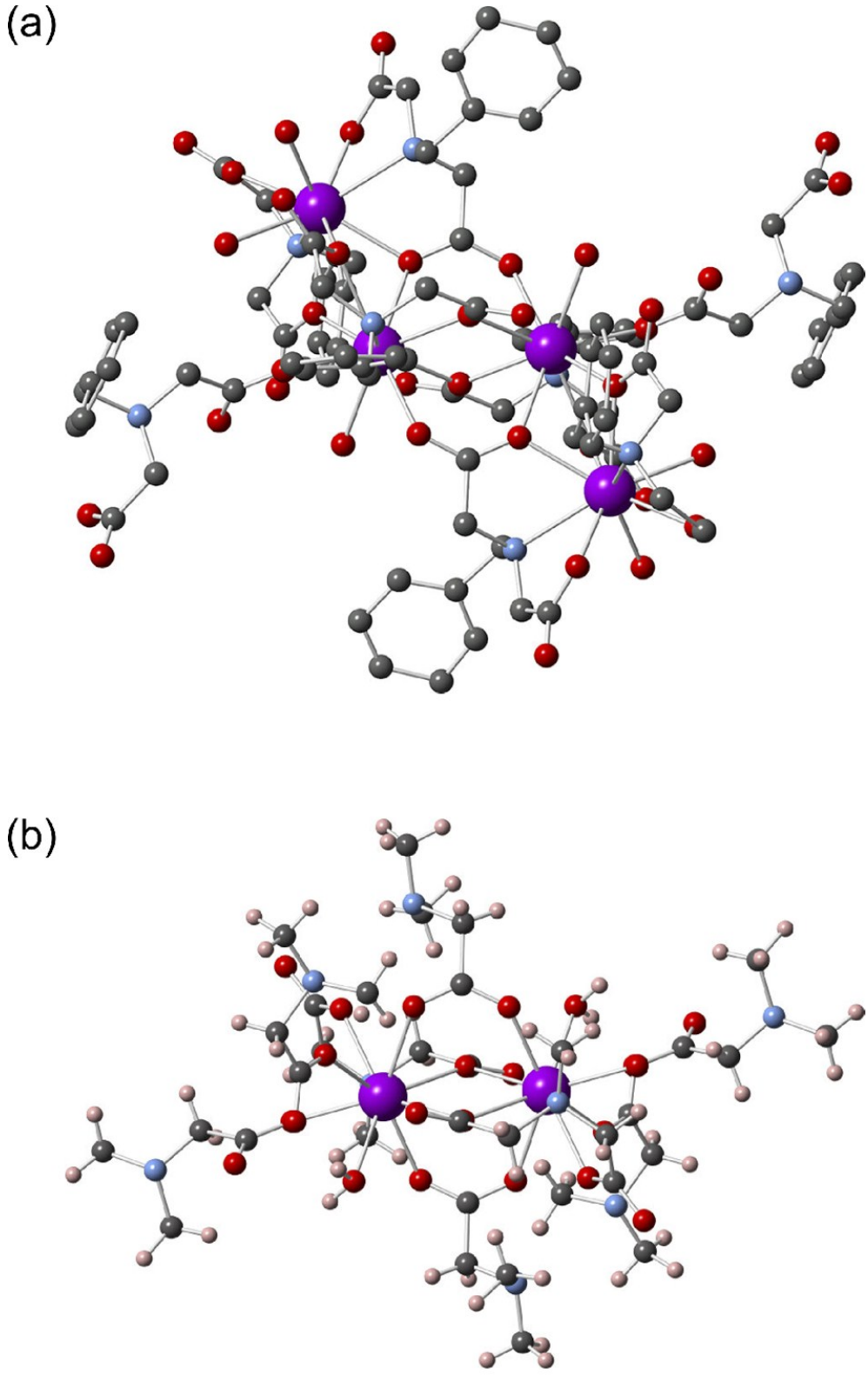


Figure S2 Scheme of the magnetic exchange interactions present in complex **6** together with a description of the pathways involved in each one of these interactions. Purple, red and grey balls represent gadolinium, oxygen and carbon atoms, respectively.

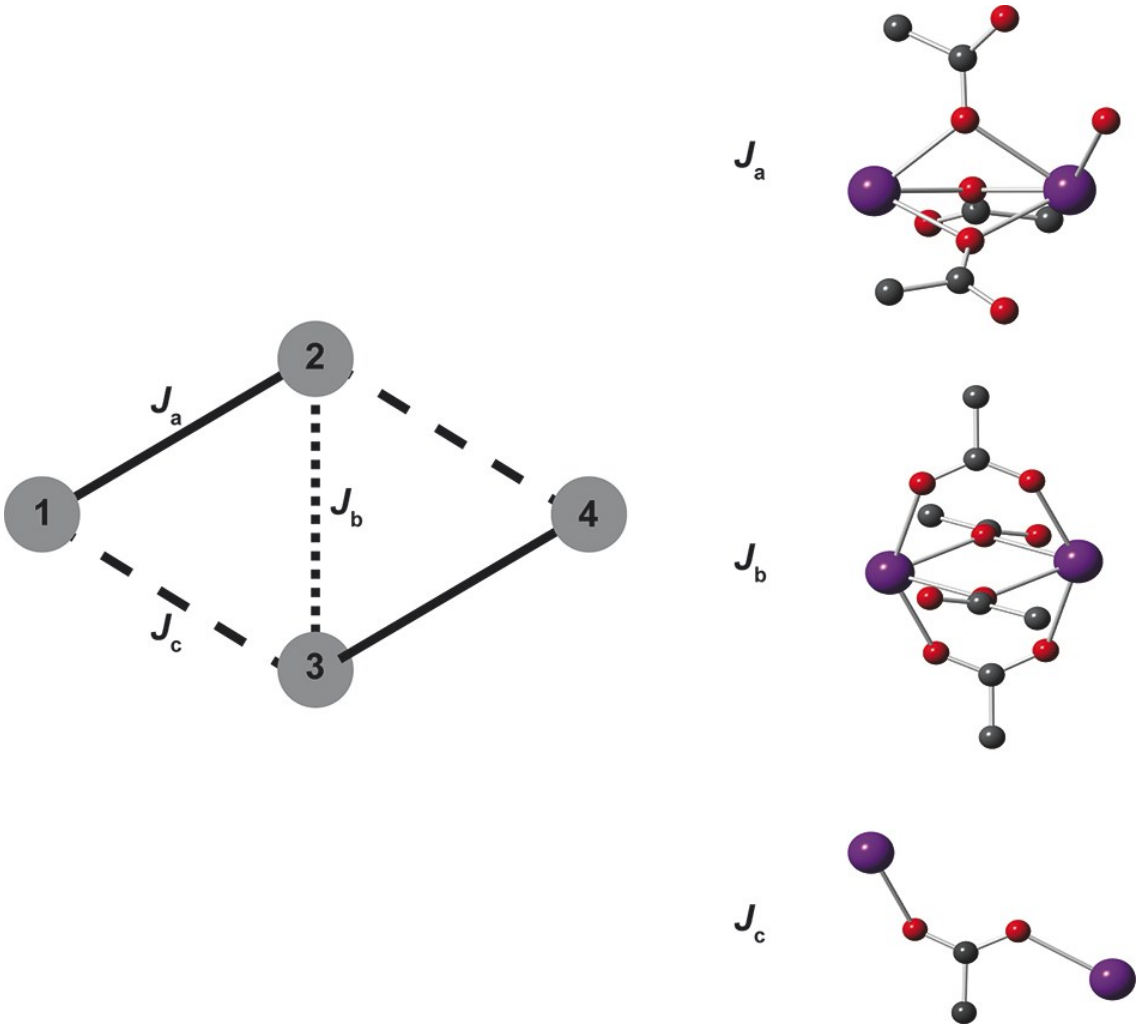


Figure S3 Species distribution diagram of the Ce-bzlida system, in 0.50 mol L^{-1} Me_4NCl at 25.0 °C (total $[Ce^{3+}]$ = 1 mmol L^{-1} and total [bzlida] = 2 mmol L^{-1}). The fully deprotonated ligand is represented as L^{2-}.

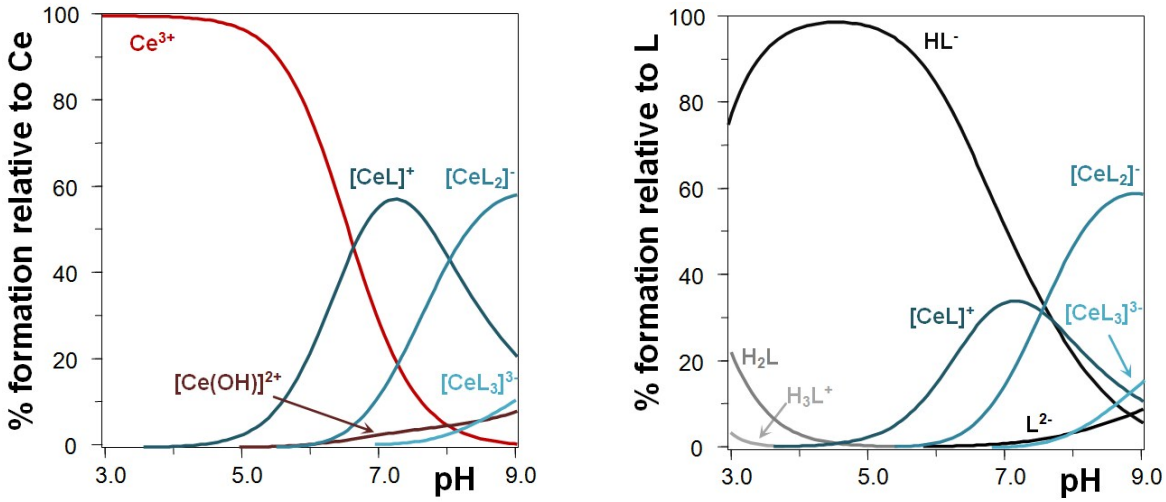


Figure S4 Species distribution diagram of the Gd-bzlida system, in 0.50 mol L^{-1} Me_4NCl at 25.0 °C (total $[Gd^{3+}]$ = 1 mmol L^{-1} and total [bzlida] = 2 mmol L^{-1}). The fully deprotonated ligand is represented as L^{2-}.

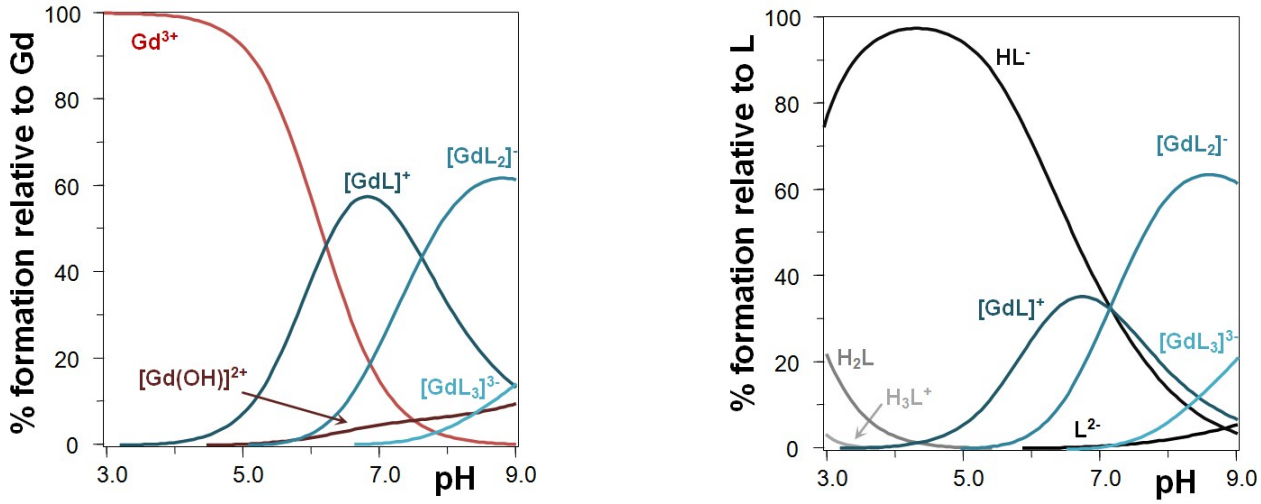
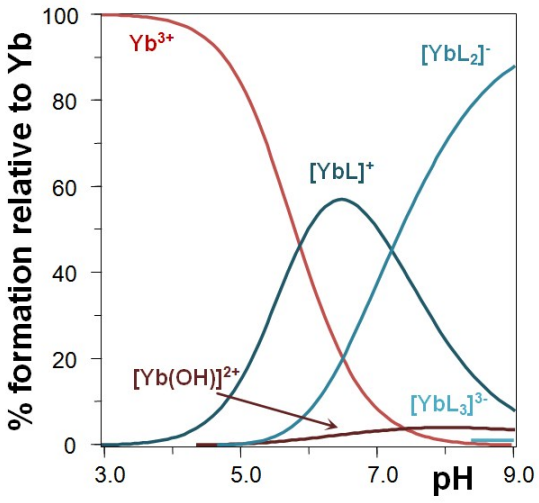


Figure S5 Species distribution diagram of the Yb-bzlida system, in 0.50 mol L^{-1} Me_4NCl at 25.0 °C (total $[Yb^{3+}]$ = 1 mmol L^{-1} and total [bzlida] = 2 mmol L^{-1}). The fully deprotonated ligand is represented as L^{2-}.



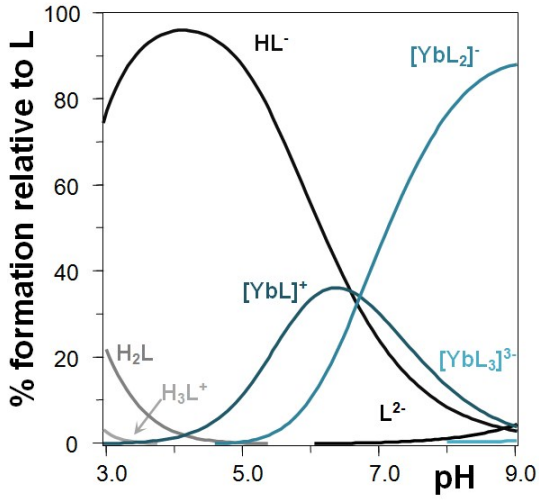


Figure S6 Thermogravimetric diagram of [La(bzlida)(Hbzlida)]·1.5H_2O (**1**). Theoretical value for water content is 4.4%.

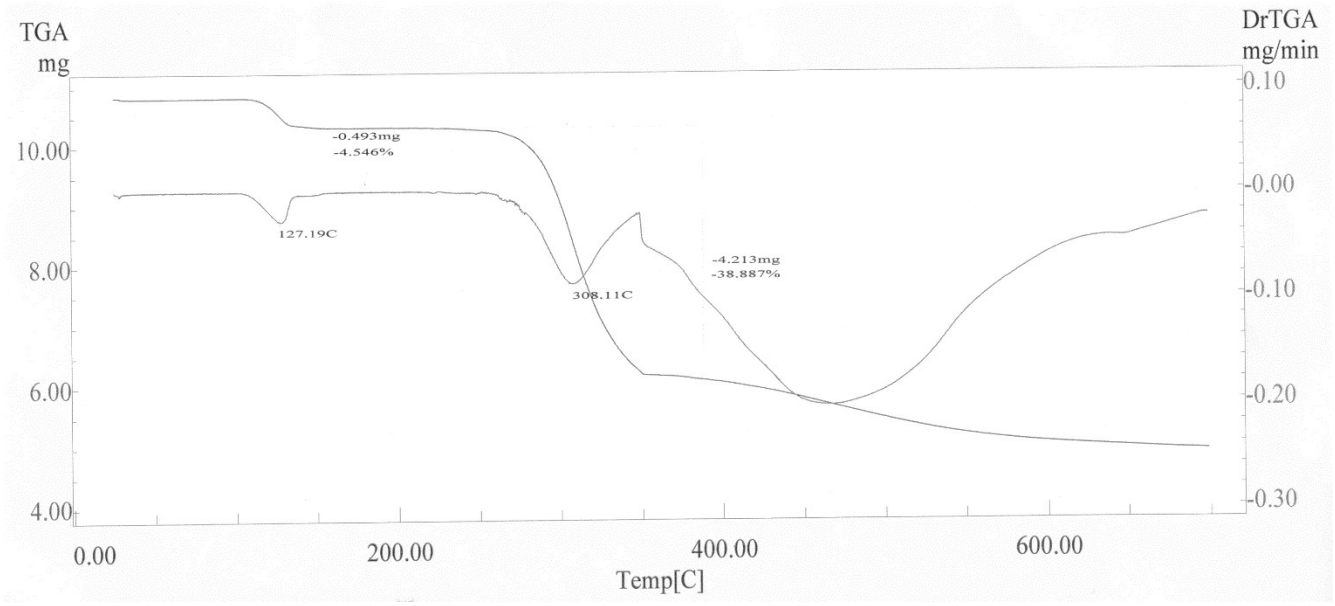


Figure S7 Thermogravimetric diagram of [Nd(bzlida)(Hbzlida)]·1.5H_2O (**2**). Theoretical value for water content is 4.4%.

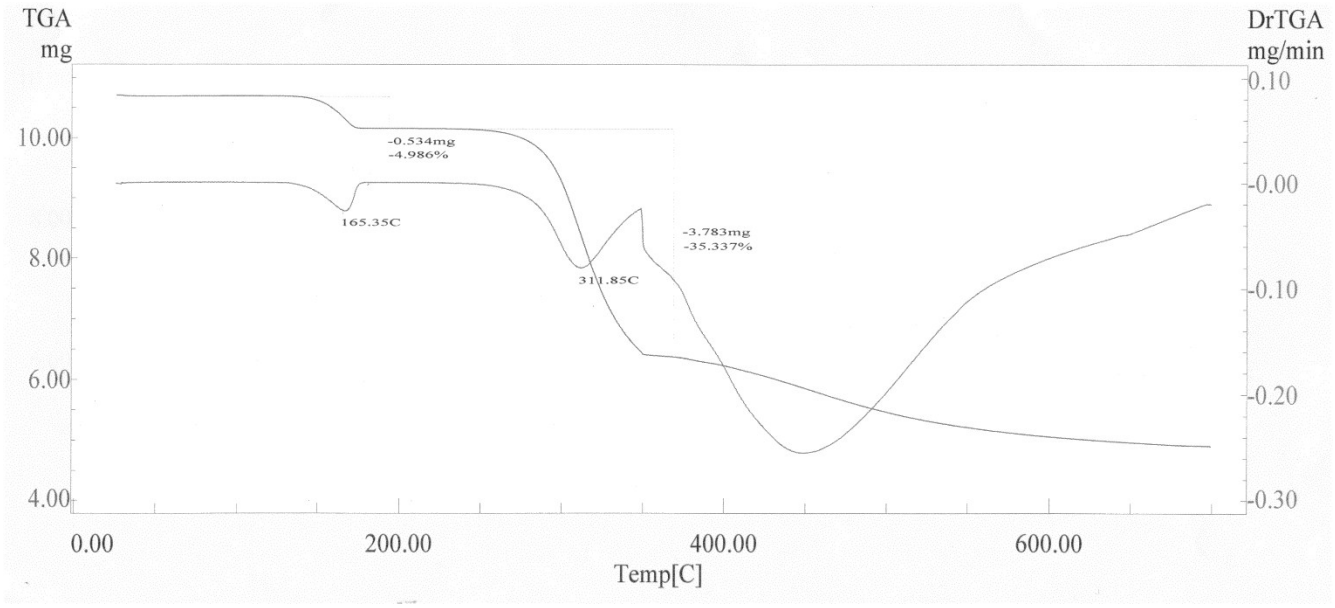


Figure S8 Thermogravimetric diagram of $[Sm_2(bzlida)_3]\cdot 3H_2O$ (**4**). Theoretical value for water content is 5.3%.

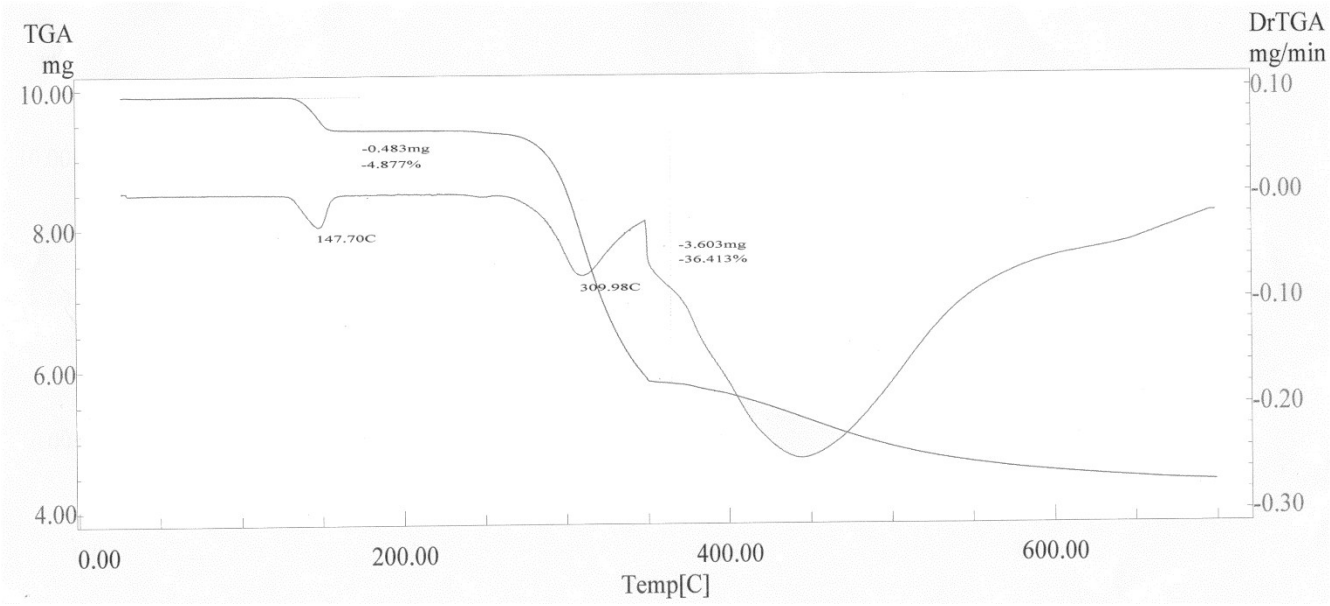


Figure S9 Thermogravimetric diagram of $[Gd_2(bzlida)_3]\cdot 3H_2O$ (**6**). Theoretical value for water content is 5.2%.

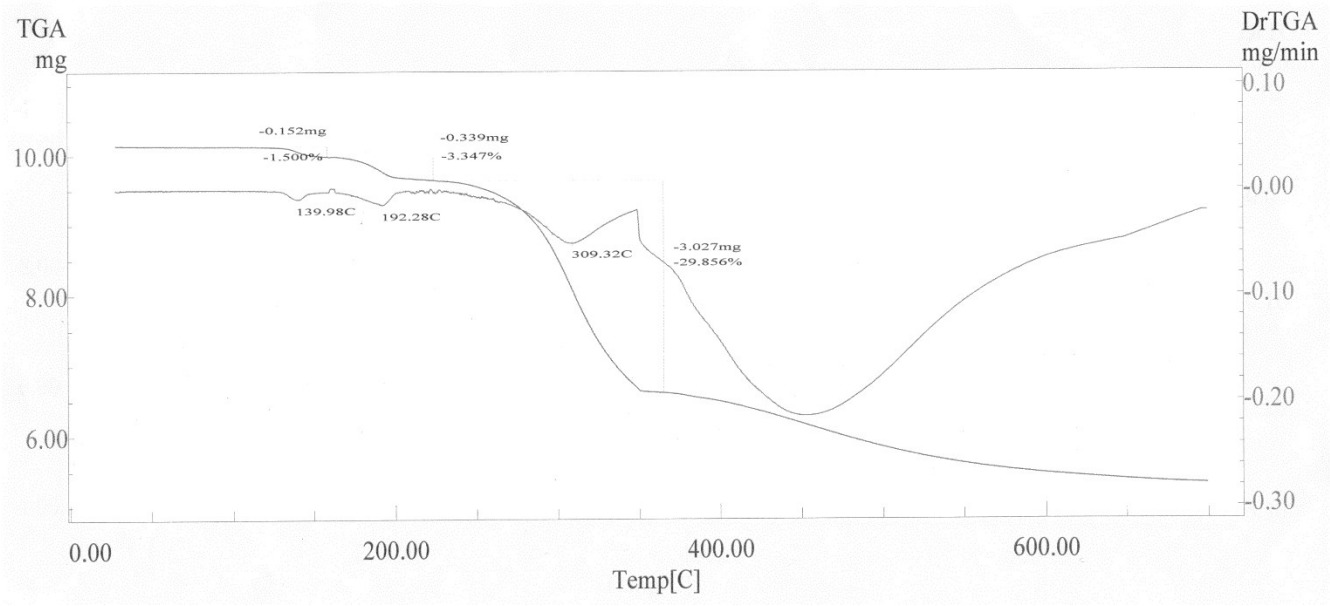


Figure S10 Powder X ray diffraction diagram of the bulk crystalline solid obtained from the hydrothermal reaction of a mixture containing H_2bzlida and Nd_2O_3 (black) compared to the calculated pattern obtained from the single crystal of $[Nd_2(bzlida)_3]\cdot 3H_2O$ (**3**), isolated from the bulk (red). Inset: overlay of XRPD of the bulk solids obtained from the reaction of H_2bzlida with La_2O_3 (1) (black) and of H_2bzlida with Nd_2O_3, (2) (blue) showing their identity.

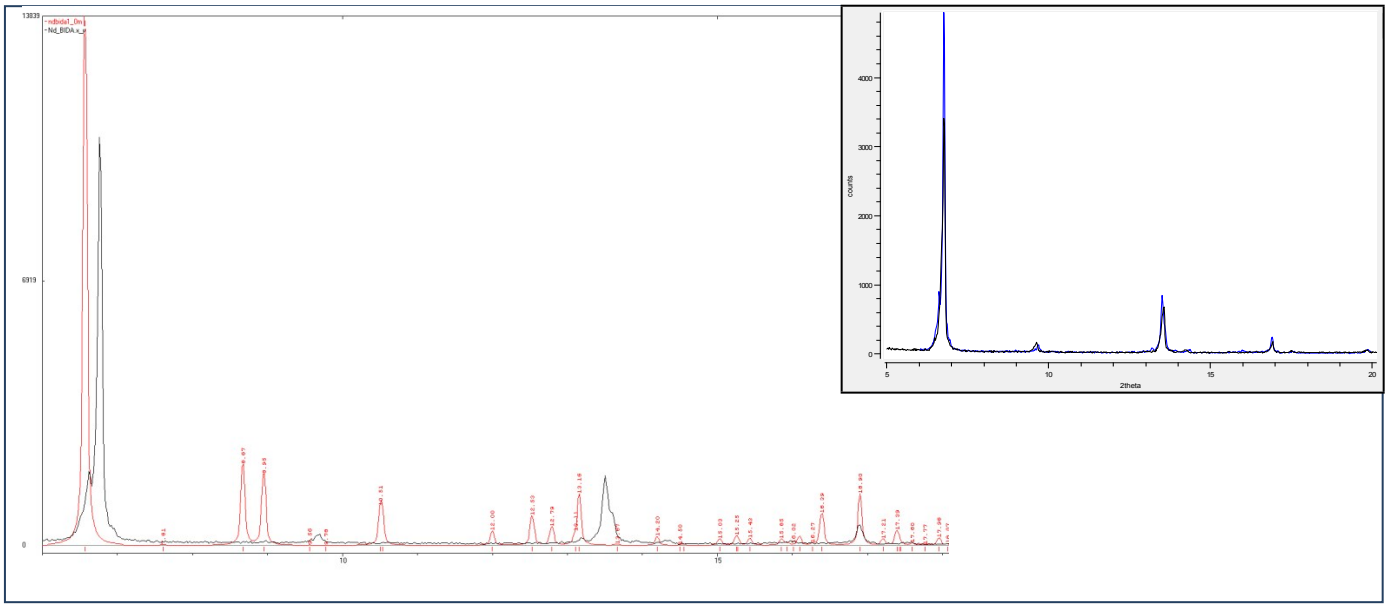


Figure S11 Hydrogen bonds between the coordinated water molecules O13, O14, O15 and the uncoordinated oxygens O2, O6, O10 in **3**.

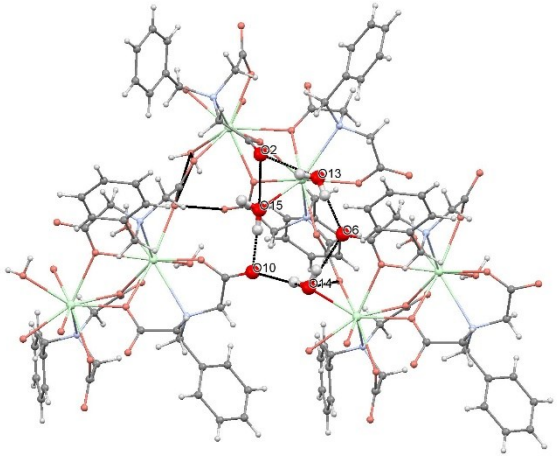


Figure S12 Top: assembly in hydrogen bonded (dotted) layers of the chains of [La(Hbzlida)(bzlida)]·H_2O; bottom: edge-on view of the layers, exposing phenyl groups at the surfaces.

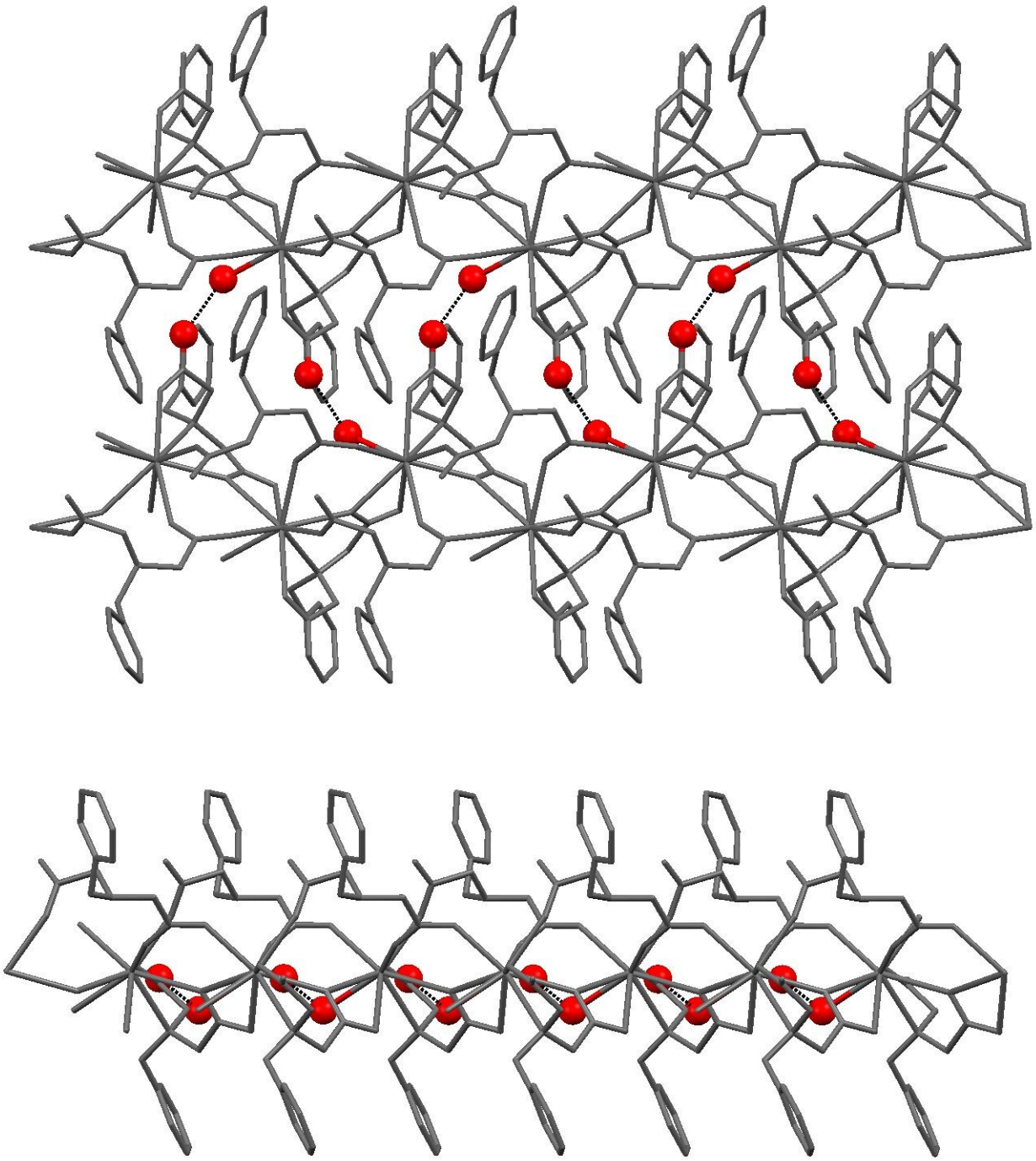


Figure S13 Hydrogen bonded layered structural arrangement in the ***ab*** plane of cations (coloured) and anions (blue) in **7**.

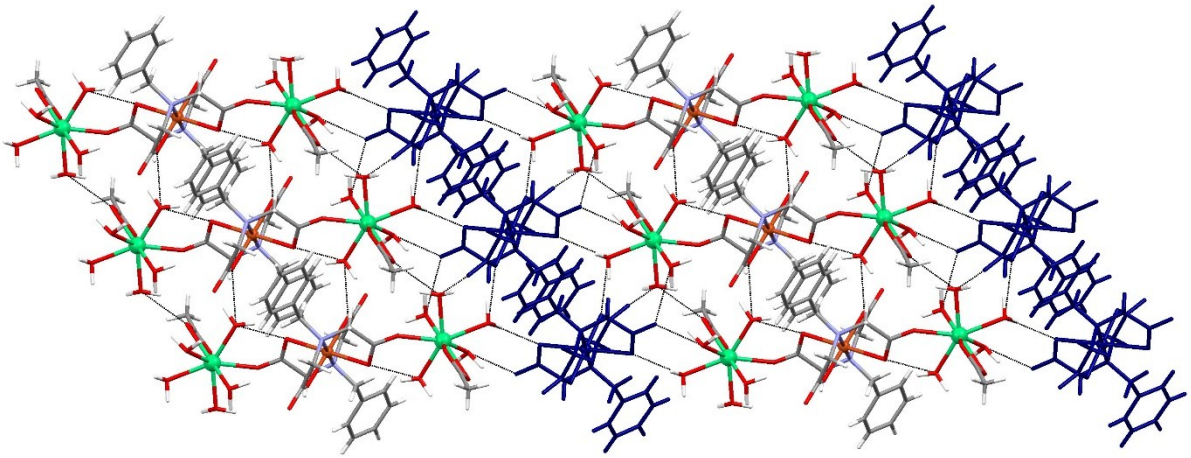


Figure S14 Location of voids hosting loosely bound water molecules in $[Cu(bzlida)_2(Er(CH_3COO)(H_2O)_5)_2]$ $[Cu(bzlida)_2]$ $6H_2O$. These voids contain the electron density equivalent to one water molecule each, but it was not possible to build or localize a molecular model of the disordered solvent.