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SUPPLEMENTARY MATERIAL

New Heterodinuclear Zn/Ln (Ln = Gd, Tb, Er, Yb) Complexes of Hexadentate *N*,*N*'-Bis(3-alkoxy-2-hydroxybenzyl)cyclohexane-1,2-diamines: Synthesis and Structure.

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Molecular structure of ***H_2L^1***

Table S1. Intramolecular hydrogen bonds /Å,° in **H_2L^1**.

D-H	A	D-H	H···A	D···A	D-H···A
O9-H9	N11	0.82	2.27	2.897(3)	134
O26-H26	N18	0.82	2.43	3.070(3)	135

Table S2. Intermolecular hydrogen bonds /Å,° in **H_2L^1**.

Symmetry operator (1/2+x,1/2-y,1-z) generates equivalent atoms that are marked with "#".

D-H	A	D-H	H···A	D···A	D-H···A
C10-H10B	O26#	0.97	2.62	3.547(4)	160
C13-H13A	O2#	0.97	2.48	3.312(4)	144
C15-H15B	O2#	0.97	2.59	3.396(5)	141
N11-H11	O9#	0.91	1.94	2.832(4)	167

Table S3. Intermolecular CH···π interactions /Å,° in **H_2L^1**.

Symmetry operator (1/2+x,1/2-y,1-z) generates equivalent atoms that are marked with "#", (-1/2+x,3/2-y,1-z) marked with "#2", (-1/2+x,1/2-y,1-z) marked with "#3". The centroids Cg1 and Cg3 represent the aromatic rings C3-C8 and C20-C25, respectively.

C-H	Cg	C-H	H···Cg	C···Cg	γ	C-H···Cg
C6-H6	Cg3#	0.93	2.85	3.60	11	138
C17-H17	Cg1#	0.98	3.19	4.15	37	167
C28-H28B	Cg3#2	0.96	2.78	3.65	10	151
N18-H18	Cg1#3	0.95	2.81	3.73	28	164

*Molecular structure of [Zn(**L**^{1})(μ-CH$_3$COO)Gd(NO$_3$)$_2$]*

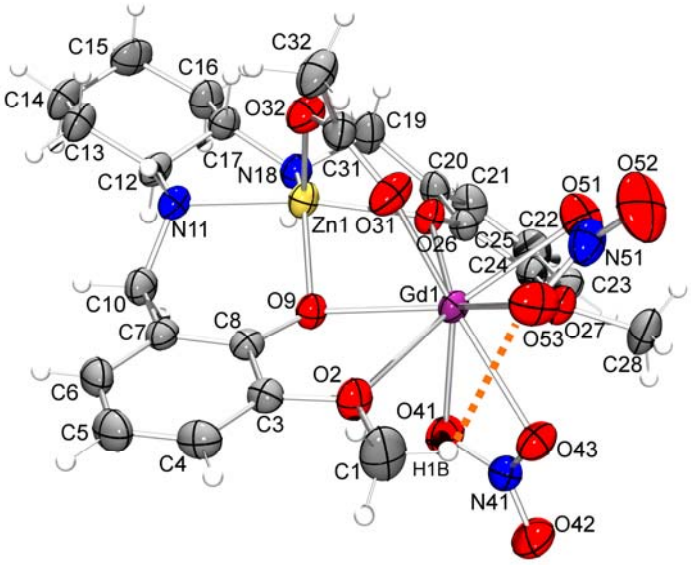

Fig. S1. Molecular structure of [Zn(**L**^{1})(μ-CH$_3$COO)Gd(NO$_3$)$_2$]. Thermal ellipsoids correspond to the 50% probability level.

Table S4. Selected bond lengths in [Zn(**L**^{1})(μ-CH$_3$COO)Gd(NO$_3$)$_2$].

Bond lengths in Å		Bond lengths in Å	
Zn1-N11	2.119(2)	Gd1-O26	2.297(2)
Zn1-N18	2.072(2)	Gd1-O27	2.559(2)
Zn1-O9	2.000(2)	Gd1-O31	2.323(2)
Zn1-O26	2.081(2)	Gd1-O41	2.512(2)
Zn1-O32	1.986(2)	Gd1-O43	2.473(2)
Gd1-O2	2.526(2)	Gd1-O51	2.484(2)
Gd1-O9	2.358(2)	Gd1-O53	2.475(2)

*Molecular structure of [Zn(**L**^{1})(μ-CH$_3$COO)Tb(NO$_3$)$_2$]*

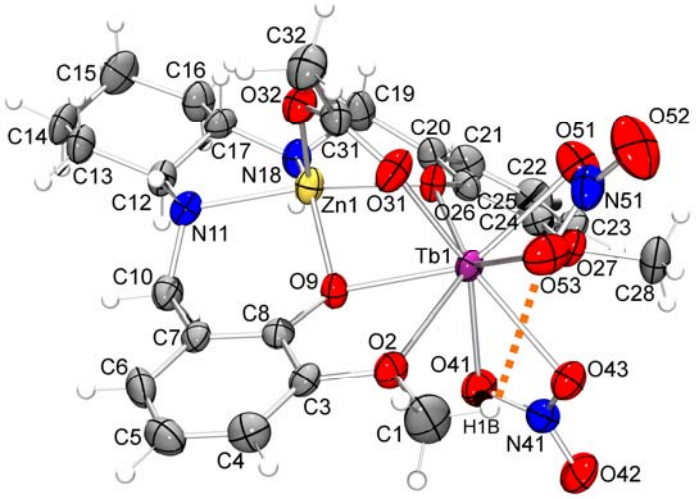

Fig. S2. Molecular structure of [Zn(**L**^{1})(μ-CH$_3$COO)Tb(NO$_3$)$_2$]. Thermal ellipsoids correspond to the 50% probability level.

Table S5. Selected bond lengths in [Zn(**L**^{1})(μ-CH$_3$COO)Tb(NO$_3$)$_2$].

Bond lengths in Å		Bond lengths in Å	
Zn1-N11	2.123(4)	Tb1-O26	2.282(3)
Zn1-N18	2.067(4)	Tb1-O27	2.558(3)
Zn1-O9	1.995(3)	Tb1-O31	2.302(4)
Zn1-O26	2.086(3)	Tb1-O41	2.500(4)
Zn1-O32	1.989(4)	Tb1-O43	2.453(4)
Tb1-O2	2.510(3)	Tb1-O51	2.470(4)
Tb1-O9	2.346(3)	Tb1-O53	2.457(4)

*Molecular structure of [Zn(**L**^{1})(μ-CH$_3$COO)Er(NO$_3$)$_2$]*

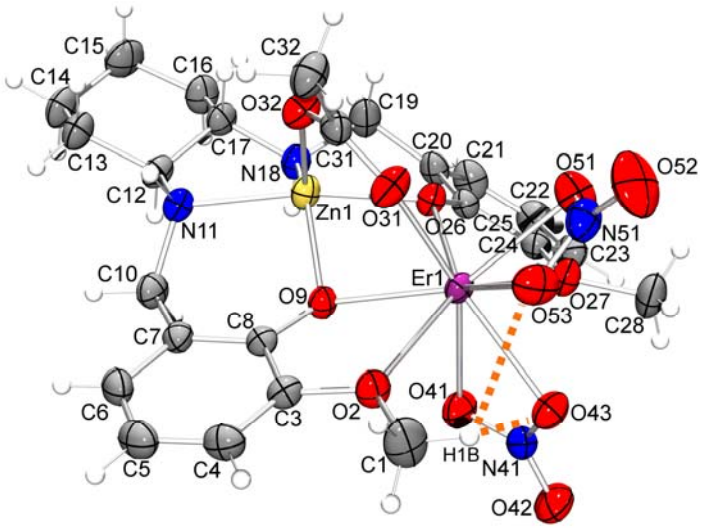

Fig. S3. Molecular structure of [Zn(**L**^{1})(μ-CH$_3$COO)Er(NO$_3$)$_2$]. Thermal ellipsoids correspond to the 50% probability level.

Table S6. Selected bond lengths in [Zn(**L**^{1})(μ-CH$_3$COO)Er(NO$_3$)$_2$].

Bond lengths in Å		Bond lengths in Å	
Zn1-N11	2.123(2)	Er1-O26	2.251(2)
Zn1-N18	2.067(2)	Er1-O27	2.544(2)
Zn1-O9	1.996(2)	Er1-O31	2.272(2)
Zn1-O26	2.083(2)	Er1-O41	2.464(2)
Zn1-O32	1.985(2)	Er1-O43	2.420(2)
Er1-O2	2.483(2)	Er1-O51	2.429(2)
Er1-O9	2.312(2)	Er1-O53	2.436(2)

*Molecular structure of [Zn(**L**^{1})(μ-CH$_3$COO)Yb(NO$_3$)$_2$]*

Table S7. Zn···Ln distances in the heterodinuclear complexes.

Complex	Zn···Ln in Å	
[Zn(**L**^{1})(μ-CH$_3$COO)Gd(NO$_3$)$_2$]	Zn1···Gd1	3.329(5)
[Zn(**L**^{1})(μ-CH$_3$COO)Tb(NO$_3$)$_2$]	Zn1···Tb1	3.317(7)
[Zn(**L**^{1})(μ-CH$_3$COO)Er(NO$_3$)$_2$]	Zn1···Er1	3.290(5)
[Zn(**L**^{1})(μ-CH$_3$COO)Yb(NO$_3$)$_2$]	Zn1···Yb1	3.274(5)
[Zn(**L**^{2})(μ-CH$_3$COO)Yb(NO$_3$)$_2$]	Zn1···Yb1	3.264(5)

Table S8. Intramolecular hydrogen bonds /Å,° in [Zn(**L**^{1})(μ-CH$_3$COO)Yb(NO$_3$)$_2$].

D-H	A	D-H	H···A	D···A	D-H···A
C1-H1B	O43	0.96	2.71	3.250(3)	116
C1-H1B	O53	0.96	2.50	3.077(4)	118
C28-H28B	O43	0.96	2.72	3.143(3)	108

Table S9. Intermolecular hydrogen bonds /Å,° in [Zn(**L**^{1})(μ-CH$_3$COO)Yb(NO$_3$)$_2$].
Symmetry operator (1-x,2-y,-z) generates equivalent atoms that are marked with "#", (1/2-x, -1/2+y,1/2-z) marked with "#2", (x,1+y,z) marked with "#3".

D-H	A	D-H	H···A	D···A	D-H···A
C10-H10A	O9#	0.97	2.60	3.418(3)	142
C10-H10B	O41#	0.97	2.62	3.343(3)	132
C13-H13A	O42#	0.97	2.66	3.375(3)	131
C28-H28C	O26#2	0.96	2.72	3.463(3)	135
N11-H11	O42#3	0.98	2.30	3.267(3)	167

Table S10. Intermolecular CH···π interactions /Å,° in [Zn(**L**[1])(μ-CH_3COO)Yb(NO_3)$_2$]. Symmetry operator (3/2-x,-1/2+y,1/2-z) generates equivalent atoms that are marked with "#", (1-x,2-y,-z) marked with "#2", (1-x,1-y,-z) marked with "#3" , (x,-1+y,z) marked with "#4" and (1/2-x,-1/2+y,1/2-z) marked with "#5". The centroids Cg4 and Cg6 represent the aromatic rings C3-C8 and C20-C25, respectively.

C-H	Cg	C-H	H···Cg	C···Cg	γ	C-H···Cg
C1-H1B	Cg4#	0.96	3.18	3.86	33	129
C10-H10A	Cg4#2	0.97	3.48	4.39	46	157
C14-H14B	Cg4#3	0.97	3.77	4.73	51	170
C15-H15A	Cg6#4	0.97	3.77	4.71	50	163
C32-H32A	Cg6#5	0.96	2.65	3.53	4	152
N18-H18	Cg4#2	0.98	2.86	3.82	26	167

*Molecular structure of [Zn(**L**^{2})(μ-CH_3COO)Yb(NO_3)$_2$]*

Table S11. Intramolecular hydrogen bonds /Å,° in [Zn(**L**^{2})(μ-CH_3COO)Yb(NO_3)$_2$].

D-H	A	D-H	H···A	D···A	D-H···A
C2-H2B	O43	0.97	2.35	3.092(4)	133
C29-H29A	O54	0.97	2.45	3.102(4)	124
C30-H30A	O42	0.96	2.63	3.364(6)	134

Table S12. Intermolecular hydrogen bonds /Å,° in [Zn(**L**^{2})(μ-CH_3COO)Yb(NO_3)$_2$]. Symmetry operator (1-x,2-y,2-z) generates equivalent atoms that are marked with "#", (3/2-x, -1/2+y,3/2-z) marked with "#2", (x,1+y,z) marked with "#3".

D-H	A	D-H	H···A	D···A	D-H···A
C11-H11A	O52#	0.97	2.54	3.280(3)	133
C11-H11B	O10#	0.97	2.62	3.401(3)	138
C30-H30C	C33#2	0.96	2.88	3.519(5)	125
N12-H12	O53#3	0.98	2.34	3.310(3)	173

Table S13. Intermolecular CH···π interactions /Å,° in [Zn(**L**^{2})(μ-CH_3COO)Yb(NO_3)$_2$]. Symmetry operator (1/2-x,-1/2+y,3/2-z) generates equivalent atoms that are marked with "#", (1-x,2-y,2-z) marked with "#2", (1-x,3-y,2-z) marked with "#3", (x,1+y,z) marked with "#4" and (3/2-x,-1/2+y,3/2-z) marked with "#5". The centroids Cg4 and Cg6 represent the aromatic rings C4-C9 and C21-C26, respectively.

C-H	Cg	C-H	H···Cg	C···Cg	γ	C-H···Cg
C1-H1B	Cg4#	0.96	3.06	3.69	21	124
C11-H11B	Cg4#2	0.97	3.36	4.29	44	160
C15-H15A	Cg4#3	0.97	3.83	4.79	54	172
C16-H16B	Cg6#4	0.97	3.68	4.60	51	160
C30-H30B	Cg6#5	0.96	3.54	4.44	41	152
C34-H34B	Cg6#5	0.96	3.04	3.80	6	137
N19-H19	Cg4#2	0.98	2.92	3.88	26	166

Crystallographic data

Table S14. Crystal and structure refinement data for **H_2L^1**, [Zn(**L^1**)(μ-CH_3COO)$Gd(NO_3)_2$] and [Zn(**L^1**)(μ-CH_3COO)$Tb(NO_3)_2$].

	H_2L^1	[Zn(**L^1**)(μ-CH_3COO)$Gd(NO_3)_2$]	[Zn(**L^1**)(μ-CH_3COO)$Tb(NO_3)_2$]
Formula	$C_{22}H_{30}N_2O_4$	$C_{24}H_{31}GdN_4O_{12}Zn$	$C_{24}H_{31}N_4O_{12}TbZn$
Crystal System	Orthorhombic	Monoclinic	Monoclinic
Space Group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a / Å	8.3018(2)	13.9038(3)	13.8892(4)
b / Å	11.2176(3)	9.8712(2)	9.8624(3)
c / Å	21.7804(5)	20.5759(4)	20.5792(6)
α / °	90	90	90
β / °	90	99.0850(10)	99.122(2)
γ / °	90	90	90
V / Å^3	2028.33(9)	2788.56(10)	2783.30(14)
d (calcd.) / g/cm^{-3}	1.266	1.882	1.890
Z	4	4	4
Diffractometer	Bruker APEX-II	Bruker APEX-II	Bruker APEX-II
Radiation (λ / Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073	Mo-Kα, 0.71073
Size / mm^3	0.44 x 0.12 x 0.08	0.34 x 0.31 x 0.16	0.10 x 0.04 x 0.03
Temperature / K	296(2)	296(2)	296(2)
θ range / °	2.04 - 26.7	1.65 - 31.16	2.88 - 27.53
Indices	$-9 \le h \le 9$	$-20 \le h \le 20$	$-18 \le h \le 14$
	$-14 \le k \le 13$	$-14 \le k \le 14$	$-12 \le k \le 12$
	$-23 \le l \le 24$	$-25 \le l \le 29$	$-26 \le l \le 26$
Reflections	21303	34773	29432
Independent reflections; R_{int}	3578 (0.0367)	8947 (0.0373)	6358 (0.0606)
Reflections ($I>2\sigma(I)$)	2753	7254	4420
data/restraints/parameters	3578/3/261	8947/0/382	6358/0/382
μ / mm^{-1}	0.087	3.288	3.453
Absorption correction	multi-scan	multi-scan	multi-scan
R indices (I_{obs} with $I>2\sigma(I)$)	$R_1 = 0.0427$, $wR_2 = 0.1046$	$R_1 = 0.0290$, $wR_2 = 0.0606$	$R_1 = 0.0388$, $wR_2 = 0.0711$
R indices (all data)	$R_1 = 0.0639$, $wR_2 = 0.1143$	$R_1 = 0.0418$, $wR_2 = 0.0648$	$R_1 = 0.0780$, $wR_2 = 0.0857$
Largest diff. peak and hole / e/Å^3	0.314 and -0.249	1.279 and -0.726	0.939 and -1.035
Goodness-of-fit on F^2	1.051	1.040	0.858
F(000)	832	1572	1576
Data collection mode	ϕ and ω scans		
Absorption correction	SADABS, Bruker 2008; SADABS, Bruker 2012		
Structure solution	direct, SHELXS-97 (Sheldrick, 2008)		
Structure refinement	Full-matrix least-squares on F^2, SHELXL-2013 (Sheldrick, 2013)		

Table S15. Crystal and structure refinement data for [Zn(**L**^{1})(μ-CH_3COO)Er(NO_3)$_2$], [Zn(**L**^{1})(μ-CH_3COO)Yb(NO_3)$_2$] and [Zn(**L**^{2})(μ-CH_3COO)Yb(NO_3)$_2$].

	[Zn(**L**^{1})(μ-CH_3COO)Er(NO_3)$_2$]	[Zn(**L**^{1})(μ-CH_3COO)Yb(NO_3)$_2$]	[Zn(**L**^{2})(μ-CH_3COO)Yb(NO_3)$_2$]
Formula	$C_{24}H_{31}ErN_4O_{12}Zn$	$C_{24}H_{31}N_4O_{12}YbZn$	$C_{26}H_{35}N_4O_{12}YbZn$
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a / Å	13.8504(5)	13.8538(2)	14.3470(8)
b / Å	9.8422(3)	9.8300(2)	10.0012(5)
c / Å	20.5575(7)	20.5847(3)	21.3948(12)
α / °	90	90	90
β / °	99.146(2)	99.2260(10)	103.556(2)
γ / °	90	90	90
V / Å^3	2766.74(16)	2767.02(8)	2984.4(3)
d (calcd.) / g/cm^{-3}	1.921	1.935	1.856
Z	4	4	4
Diffractometer	Bruker APEX-II	Bruker APEX-II	Bruker APEX-II
Radiation (λ / Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073	Mo-Kα, 0.71073
Size / mm^3	0.29 x 0.18 x 0.07	0.26 x 0.21 x 0.06	0.29 x 0.21 x 0.08
Temperature / K	296(2)	296(2)	296(2)
θ range / °	1.66 - 32.66	1.92 - 31.02	1.95- 32.87
Indices	$-18 \le h \le 21$	$-17 \le h \le 19$	$-20 \le h \le 21$
	$-14 \le k \le 11$	$-11 \le k \le 13$	$-15 \le k \le 14$
	$-31 \le l \le 30$	$-29 \le l \le 27$	$-32 \le l \le 32$
Reflections	42651	32292	50144
Independent reflections; R_{int}	10081 (0.0294)	8382 (0.0224)	10937 (0.0341)
Reflections ($I>2\sigma(I)$)	7996	6957	8538
data/restraints/parameters	10081/0/382	8382 /0/382	10937/0/400
μ / mm^{-1}	3.950	4.297	3.987
Absorption correction	multi-scan	multi-scan	multi-scan
R indices (I_{obs} with $I>2\sigma(I)$)	$R_1 = 0.0293$, $wR_2 = 0.0596$	$R_1 = 0.0252$, $wR_2 = 0.0496$	$R_1 = 0.0307$, $wR_2 = 0.0651$
R indices (all data)	$R_1 = 0.0458$, $wR_2 = 0.0647$	$R_1 = 0.0357$ $wR_2 = 0.0522$	$R_1 = 0.0467$, $wR_2 = 0.0706$
Largest diff. peak and hole / e/Å^3	1.648 and -0.685	1.413 and -0.820	1.584 and -0.823
Goodness-of-fit on F^2	1.016	1.074	1.026
F(000)	1588	1596	1660
Data collection mode	ϕ and ω scans		
Absorption correction	SADABS, Bruker 2012; SADABS, Bruker 2008		
Structure solution	direct, SHELXS-97 (Sheldrick, 2008)		
Structure refinement	Full-matrix least-squares on F^2, SHELXL-2013 (Sheldrick, 2013)		