

Supporting Information

A Series of Trinuclear Ni^{II}Ln^{III}Ni^{II} Complexes Derived from 2,6-Di(acetoacetyl)pyridine:
Synthesis, Structure and Magnetism

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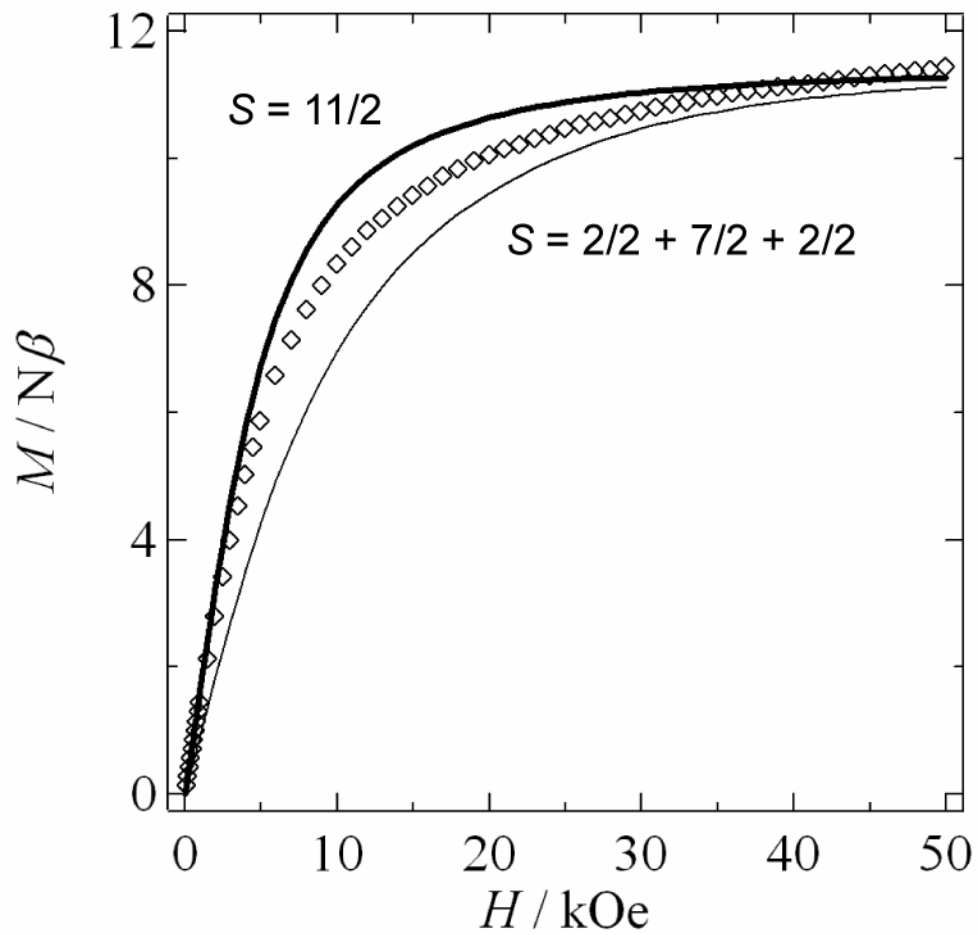


Figure S1. M vs. H curve for $7'$. The thick and thin lines are the theoretical curves for $S = 11/2$ and $S = (2/2 + 7/2 + 2/2)$, respectively, drawn using $g_{\text{ave.}} = 2.06$.

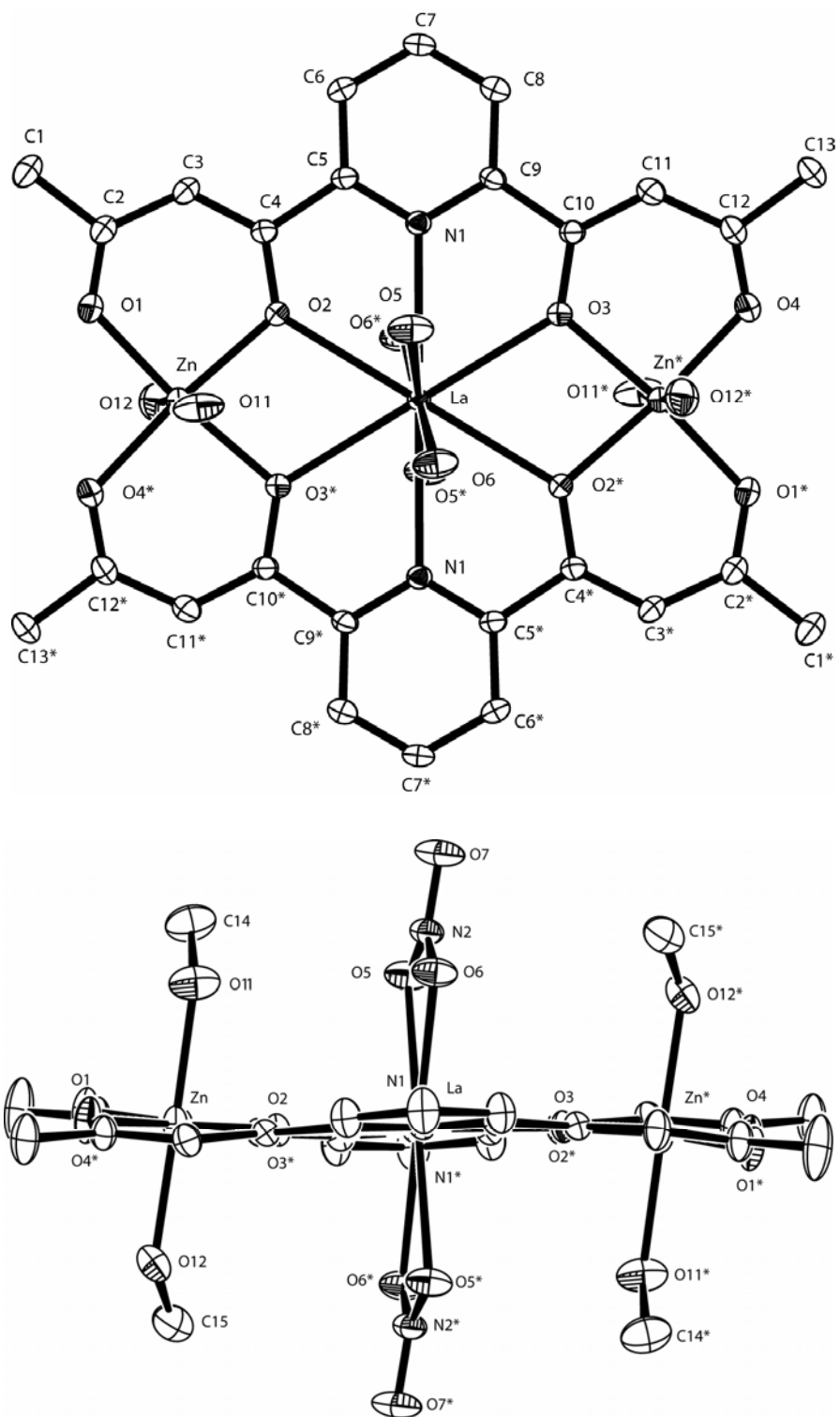


Figure S2. ORTEP drawings of Zn_2La complex.

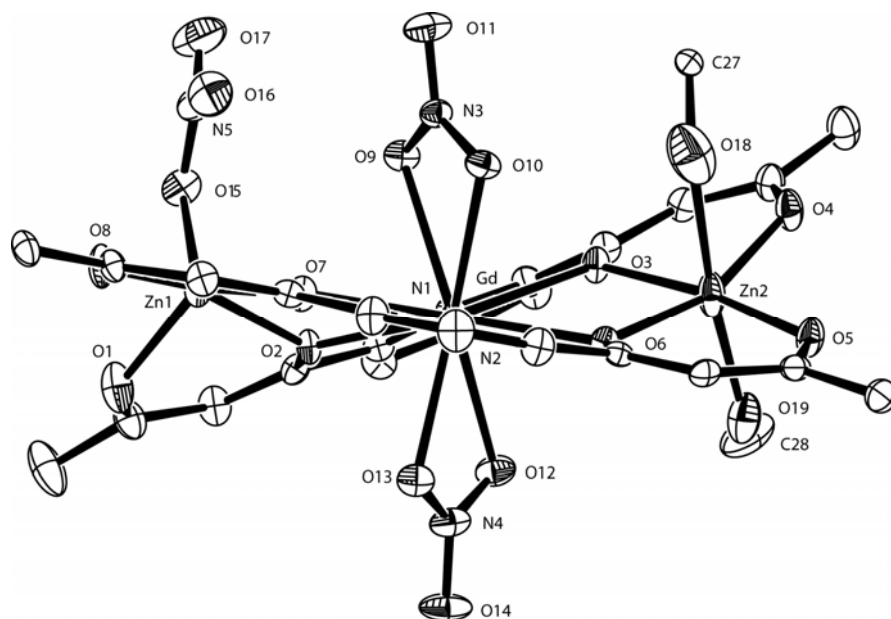
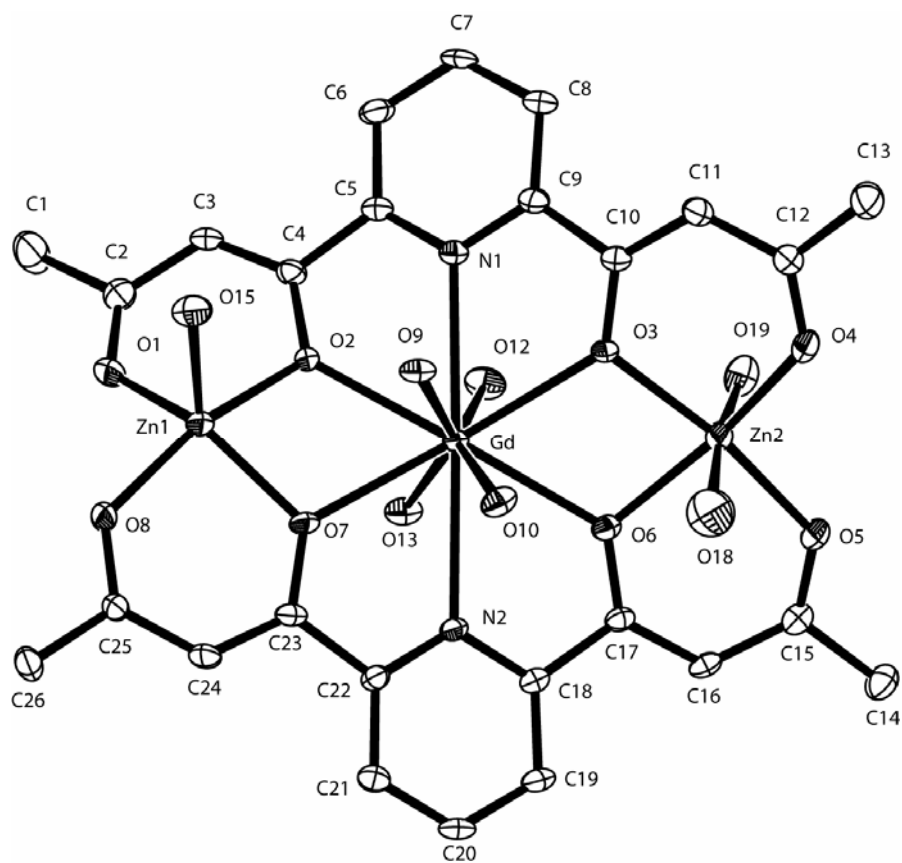


Figure S3. ORTEP drawings of Zn₂Gd complex.

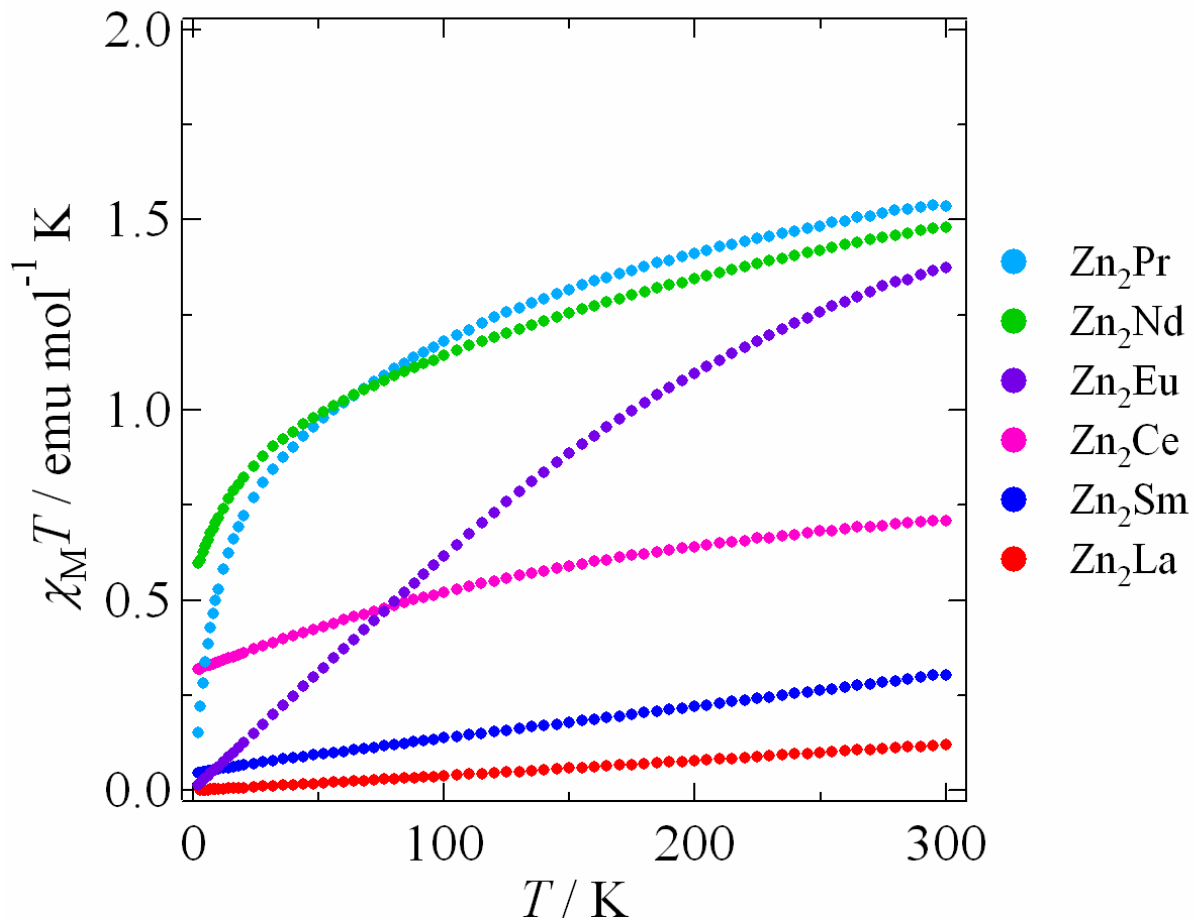


Figure S4. $\chi_M T$ vs. T plots for Zn₂Ln complexes. Zn₂La (red), Zn₂Ce (pink), Zn₂Pr (light-blue), Zn₂Nd (greenish-yellow), Zn₂Sm (blue), Zn₂Eu (purple).

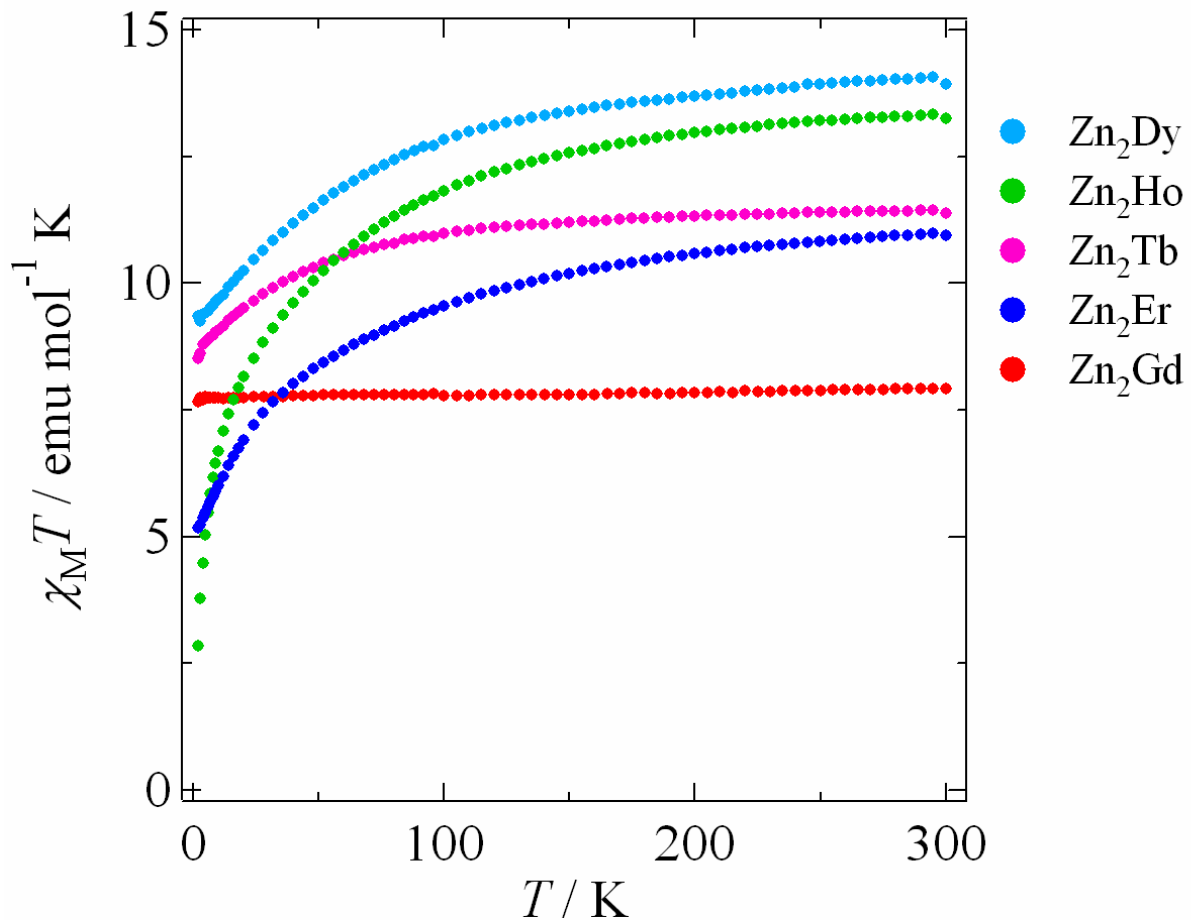


Figure S5. $\chi_M T$ vs. T plots for Zn₂Ln complexes. Zn₂Gd (red), Zn₂Tb (pink), Zn₂Dy (light-blue), Zn₂Ho (greenish-yellow), Zn₂Er (blue).

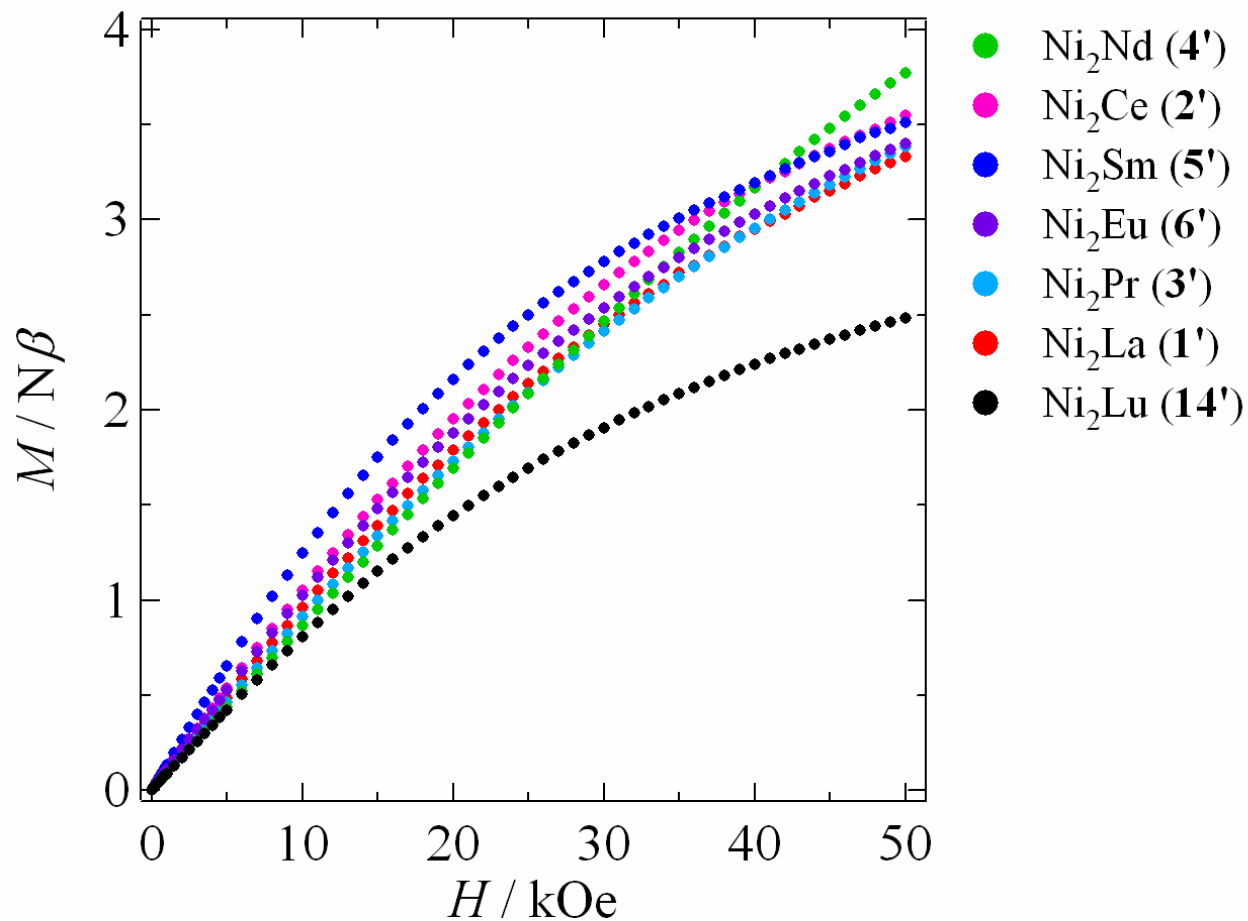


Figure S6. M vs. H curve for complexes **1'** – **6'** and **14'**. **1'** (red), **2'** (pink), **3'** (light-blue), **4'** (greenish-yellow), **5'** (blue), **6'** (purple), **14'** (black).

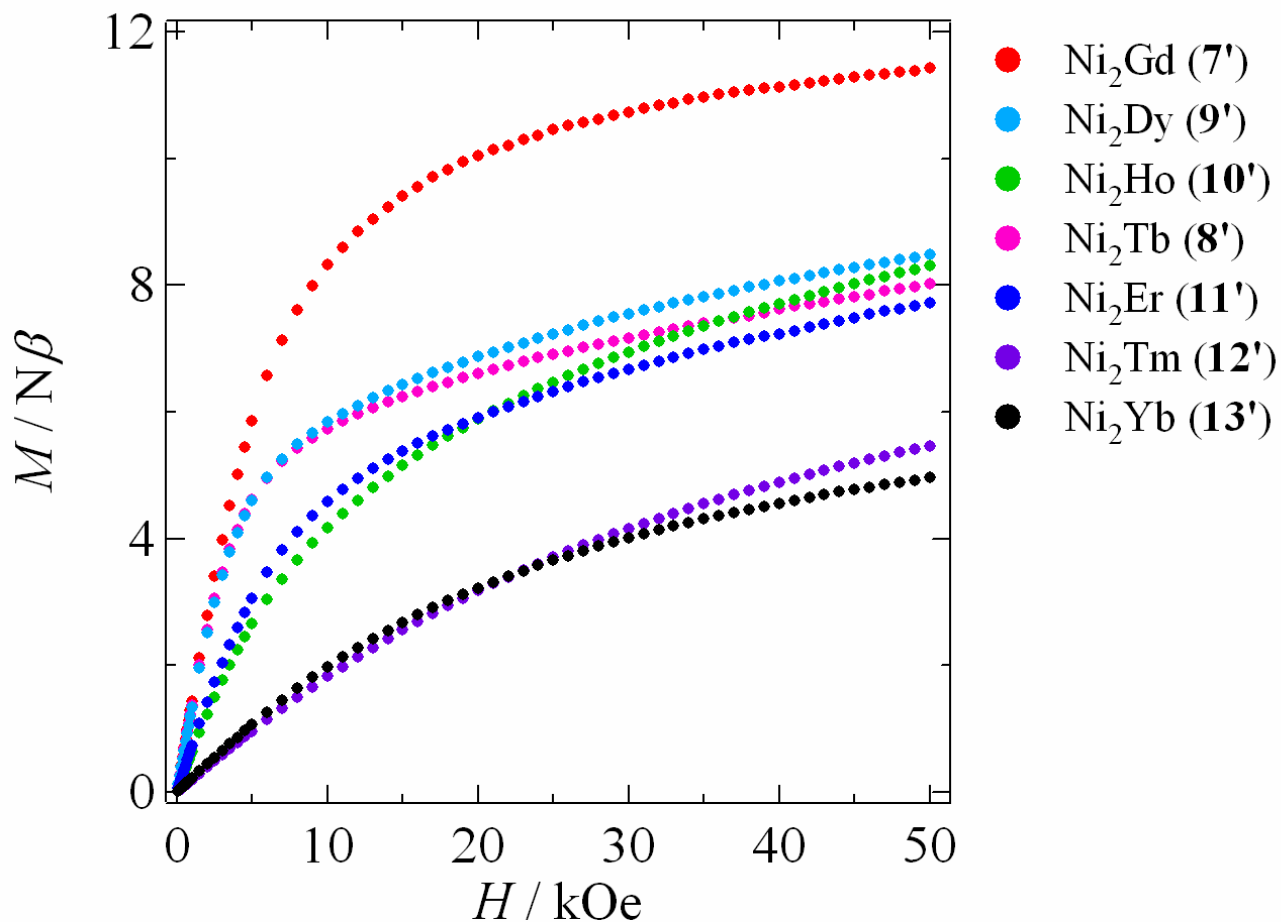


Figure S7. M vs. H curve for complexes **7'** – **13'**. **7'** (red), **8'** (pink), **9'** (light-blue), **10'** (greenish-yellow), **11'** (blue), **12'** (purple), **13'** (black).

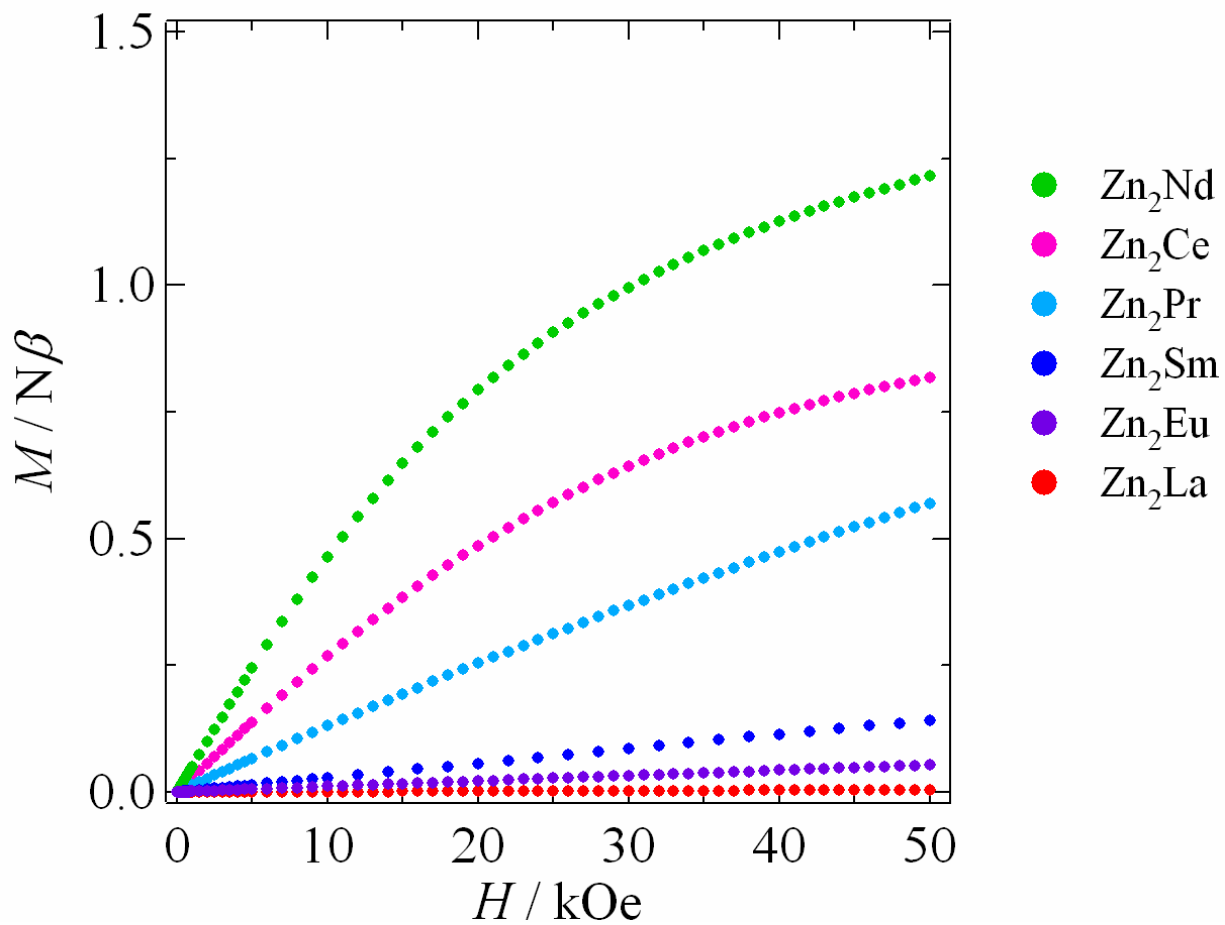


Figure S8. M vs. H curve for Zn_2Ln complexes. Zn_2La (red), Zn_2Ce (pink), Zn_2Pr (light-blue), Zn_2Nd (greenish-yellow), Zn_2Sm (blue), Zn_2Eu (purple).

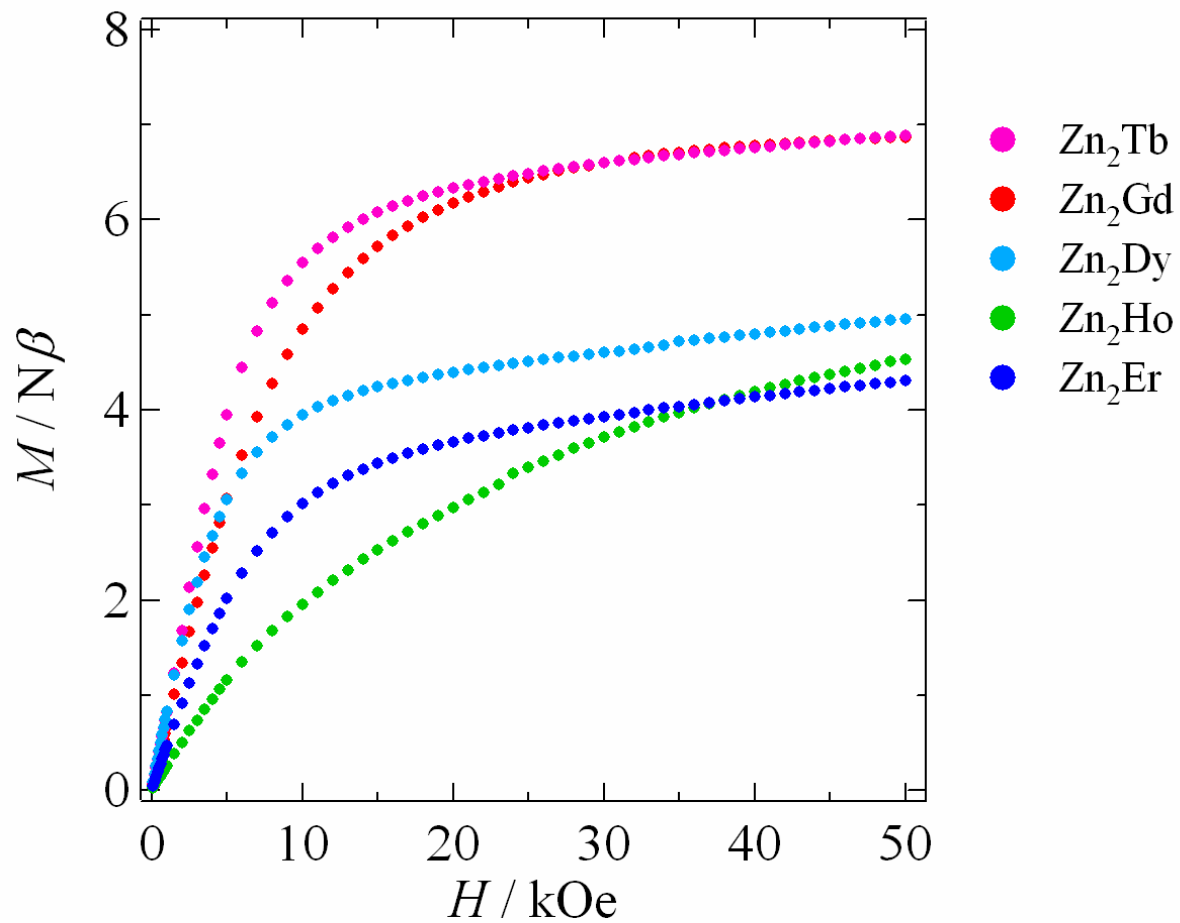


Figure S9. M vs. H curve for Zn_2Ln complexes. Zn_2Gd (red), Zn_2Tb (pink), Zn_2Dy (light-blue), Zn_2Ho (greenish-yellow), Zn_2Er (blue).

Table S1. Crystal parameters for complexes **1 - 14**.

Comp.	Space group	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	α / deg	β / deg	γ / deg	<i>V</i> / Å ³	<i>D_c</i> / g cm ⁻³	<i>R</i> 1 ^a	<i>R</i> ^b	<i>R</i> w ^c
1	<i>P</i> $\bar{1}$	7.8700(4)	9.4406(4)	14.5086(5)	92.775(2)	104.760(2)	91.309(3)	1040.47(8)	1.744	0.028	0.051	0.097
2	<i>P</i> $\bar{1}$	7.8217(2)	9.4165(3)	14.5053(5)	92.707(2)	104.827(2)	91.333(1)	1030.94(6)	1.762	0.029	0.055	0.086
3	<i>P</i> $\bar{1}$	7.8083(7)	9.3987(6)	14.481(1)	92.794(2)	104.708(4)	91.285(3)	1026.0(1)	1.774	0.028	0.057	0.087
4	<i>P</i> $\bar{1}$	7.8223(6)	9.3897(8)	14.454(1)	92.480(3)	104.616(3)	91.396(4)	1025.6(1)	1.778	0.032	0.061	0.090
5-A	<i>P</i> $\bar{1}$	7.8113(3)	9.3785(5)	14.4618(7)	92.432(3)	104.463(3)	91.265(2)	1024.35(8)	1.794	0.027	0.051	0.091
6-A	<i>P</i> $\bar{1}$	7.7920(6)	9.3695(8)	14.451(1)	92.424(2)	104.477(4)	91.207(3)	1020.1(1)	1.800	0.026	0.047	0.075
7-A	<i>P</i> $\bar{1}$	7.8220(4)	9.3686(5)	14.4871(9)	92.321(3)	104.321(3)	91.211(2)	1027.26(9)	1.790	0.034	0.056	0.091
5-B	<i>P</i> $\bar{1}$	7.8897(8)	16.801(1)	16.981(2)	68.735(2)	77.850(2)	78.293(5)	2030.8(3)	1.819	0.052	0.094	0.170
6-B	<i>P</i> $\bar{1}$	7.8330(7)	16.713(1)	16.9108(9)	68.641(2)	78.020(4)	78.468(2)	1998.1(3)	1.852	0.045	0.069	0.131
7-B	<i>P</i> $\bar{1}$	7.9047(8)	16.786(2)	17.040(2)	68.804(6)	78.224(4)	78.643(4)	2044.8(3)	1.818	0.038	0.064	0.135
7-C	<i>C</i> 2/ <i>c</i>	14.103(1)	17.2153(9)	16.3096(8)	–	99.328(3)	–	3907.5(4)	1.835	0.047	0.085	0.066
8	<i>C</i> 2/ <i>c</i>	14.1121(5)	17.2313(6)	16.3004(6)	–	99.2495(9)	–	3912.2(2)	1.835	0.033	0.059	0.095
9	<i>C</i> 2/ <i>c</i>	14.0708(6)	17.2309(9)	16.2927(9)	–	99.187(1)	–	3899.5(3)	1.844	0.030	0.054	0.104
10	<i>P</i> $\bar{1}$	10.862(2)	14.851(3)	16.521(3)	109.156(4)	100.149(6)	110.336(7)	2230.3(7)	1.756	0.063	0.107	0.202
11	<i>P</i> $\bar{1}$	10.8507(6)	14.8700(6)	16.5020(8)	109.139(2)	100.197(2)	110.294(2)	2228.6(2)	1.760	0.038	0.064	0.131
12	<i>P</i> $\bar{1}$	10.8582(1)	14.8577(1)	16.5084(2)	109.1785(7)	100.1183(7)	110.2845(8)	2229.85(4)	1.762	0.033	0.057	0.110
13	<i>P</i> $\bar{1}$	10.8743(5)	14.8551(6)	16.5024(9)	108.984(2)	100.109(1)	110.412(3)	2233.4(2)	1.765	0.050	0.075	0.148
14	<i>P</i> $\bar{1}$	10.8349(7)	14.809(2)	16.448(2)	109.124(3)	100.140(3)	110.188(5)	2212.4(4)	1.785	0.030	0.049	0.094

G. O. F = 1.00 for all compounds, ^a *R*1 ($I > 2.0\sigma(I)$) = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, ^b *R* (all obsd.) = $\Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$,

^c *R*w (all obsd.) = $[\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma w|F_o^2|^2]^{1/2}$

Table S2 Selected bond distances of **1 – 14**.

Ni₂La(1)					
La	O(2)	2.578(2)	La	O(2) ¹⁾	2.578(2)
La	O(3)	2.562(2)	La	O(3) ¹⁾	2.562(2)
La	O(5)	2.616(2)	La	O(5) ¹⁾	2.616(2)
La	O(6)	2.618(2)	La	O(6) ¹⁾	2.618(2)
La	N(1)	2.763(2)	La	N(1) ¹⁾	2.763(2)
Ni	O(1)	1.981(2)	Ni	O(2)	2.007(2)
Ni	O(3) ¹⁾	2.009(2)	Ni	O(4) ¹⁾	1.978(2)
Ni	O(11)	2.101(3)	Ni	O(12)	2.104(3)
Ni₂Ce(2)					
Ce	O(2)	2.565(2)	Ce	O(2) ¹⁾	2.565(2)
Ce	O(3)	2.547(2)	Ce	O(3) ¹⁾	2.547(2)
Ce	O(5)	2.589(2)	Ce	O(5) ¹⁾	2.589(2)
Ce	O(6)	2.591(2)	Ce	O(6) ¹⁾	2.591(2)
Ce	N(1)	2.753(2)	Ce	N(1) ¹⁾	2.753(2)
Ni	O(1)	1.986(2)	Ni	O(2)	2.007(2)
Ni	O(3) ¹⁾	2.015(2)	Ni	O(4) ¹⁾	1.981(2)
Ni	O(11)	2.104(2)	Ni	O(12)	2.102(2)
Ni₂Pr(3)					
Pr	O(2)	2.553(2)	Pr	O(2) ¹⁾	2.553(2)
Pr	O(3)	2.539(2)	Pr	O(3) ¹⁾	2.539(2)
Pr	O(5)	2.569(2)	Pr	O(5) ¹⁾	2.569(2)
Pr	O(6)	2.567(2)	Pr	O(6) ¹⁾	2.567(2)
Pr	N(1)	2.740(2)	Pr	N(1) ¹⁾	2.740(2)
Ni	O(1)	1.982(2)	Ni	O(2)	2.002(2)
Ni	O(3) ¹⁾	2.007(2)	Ni	O(4) ¹⁾	1.980(2)
Ni	O(11)	2.099(2)	Ni	O(12)	2.104(2)
Ni₂Nd(4)					
Nd	O(2)	2.545(2)	Nd	O(2) ¹⁾	2.545(2)
Nd	O(3)	2.529(2)	Nd	O(3) ¹⁾	2.529(2)
Nd	O(5)	2.548(2)	Nd	O(5) ¹⁾	2.548(2)
Nd	O(6)	2.551(2)	Nd	O(6) ¹⁾	2.551(2)
Nd	N(1)	2.736(2)	Nd	N(1) ¹⁾	2.736(2)
Ni	O(1)	1.980(2)	Ni	O(2)	2.001(2)
Ni	O(3) ¹⁾	2.006(2)	Ni	O(4) ¹⁾	1.975(2)
Ni	O(11)	2.101(3)	Ni	O(12)	2.097(3)
Ni₂Sm(5-A)					
Sm	O(2)	2.539(2)	Sm	O(2) ¹⁾	2.539(2)
Sm	O(3)	2.517(2)	Sm	O(3) ¹⁾	2.517(2)
Sm	O(5)	2.513(2)	Sm	O(5) ¹⁾	2.513(2)
Sm	O(6)	2.518(2)	Sm	O(6) ¹⁾	2.518(2)
Sm	N(1)	2.723(2)	Sm	N(1) ¹⁾	2.723(2)
Ni	O(1)	1.983(2)	Ni	O(2)	1.997(2)
Ni	O(3)	2.006(2)	Ni	O(4)	1.977(2)
Ni	O(8)	2.102(3)	Ni	O(9)	2.101(3)

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Ni₂Sm(5-B)

Sm	O(2)	2.529(3)	Sm	O(3)	2.527(3)
Sm	O(6)	2.499(3)	Sm	O(7)	2.510(3)
Sm	O(9)	2.525(4)	Sm	O(10)	2.516(4)
Sm	O(12)	2.499(3)	Sm	O(13)	2.497(3)
Sm	N(1)	2.690(4)	Sm	N(2)	2.667(4)
Ni(1)	O(1)	1.997(4)	Ni(1)	O(2)	2.000(3)
Ni(1)	O(7)	2.015(3)	Ni(1)	O(8)	1.995(4)
Ni(1)	O(18)	2.076(4)	Ni(1)	O(19)	2.082(4)
Ni(2)	O(3)	2.015(3)	Ni(2)	O(4)	1.986(3)
Ni(2)	O(5)	1.982(3)	Ni(2)	O(6)	2.003(3)
Ni(2)	O(20)	2.121(4)	Ni(2)	O(21)	2.069(3)

Ni₂Eu(6-A)

Eu	O(2)	2.532(2)	Eu	O(2) ¹⁾	2.532(2)
Eu	O(3)	2.506(2)	Eu	O(3) ¹⁾	2.506(2)
Eu	O(5)	2.506(2)	Eu	O(5) ¹⁾	2.506(2)
Eu	O(6)	2.495(2)	Eu	O(6) ¹⁾	2.495(2)
Eu	N(1)	2.719(2)	Eu	N(1) ¹⁾	2.719(2)
Ni	O(1)	1.979(2)	Ni	O(2)	1.992(2)
Ni	O(3)1)	2.006(2)	Ni	O(4) ¹⁾	1.969(2)
Ni	O(11)	2.103(2)	Ni	O(12)	2.098(2)

Ni₂Eu(6-B)

Eu	O(2)	2.514(4)	Eu	O(3)	2.508(3)
Eu	O(6)	2.484(3)	Eu	O(7)	2.496(3)
Eu	O(9)	2.493(4)	Eu	O(10)	2.490(4)
Eu	O(12)	2.468(4)	Eu	O(13)	2.475(4)
Eu	N(1)	2.678(4)	Eu	N(2)	2.657(4)
Ni(1)	O(1)	1.998(5)	Ni(1)	O(2)	1.999(4)
Ni(1)	O(7)	2.022(4)	Ni(1)	O(8)	1.989(4)
Ni(1)	O(18)	2.066(4)	Ni(1)	O(19)	2.068(5)
Ni(2)	O(3)	2.014(3)	Ni(2)	O(4)	1.986(4)
Ni(2)	O(5)	1.980(4)	Ni(2)	O(6)	1.993(3)
Ni(2)	O(20)	2.111(4)	Ni(2)	O(21)	2.062(4)

Ni₂Gd(7-A)

Gd	O(2)	2.542(2)	Gd	O(2) ¹⁾	2.542(2)
Gd	O(3)	2.506(3)	Gd	O(3) ¹⁾	2.506(3)
Gd	O(5)	2.502(3)	Gd	O(5) ¹⁾	2.502(3)
Gd	O(6)	2.493(3)	Gd	O(6) ¹⁾	2.493(3)
Gd	N(1)	2.719(3)	Gd	N(1) ¹⁾	2.719(3)
Ni	O(1)	1.981(3)	Ni	O(2)	1.992(3)
Ni	O(3) ¹⁾	2.004(3)	Ni	O(4) ¹⁾	1.976(3)
Ni	O(11)	2.107(3)	Ni	O(12)	2.101(3)

Ni₂Gd(7-B)

Gd	O(2)	2.523(3)	Gd	O(3)	2.529(3)
Gd	O(6)	2.485(3)	Gd	O(7)	2.513(3)
Gd	O(9)	2.495(3)	Gd	O(10)	2.501(3)
Gd	O(12)	2.459(3)	Gd	O(13)	2.477(3)
Gd	N(1)	2.680(3)	Gd	N(2)	2.670(3)

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Ni(1) O(1)	2.007(4)	Ni(1) O(2)	2.017(3)
Ni(1) O(7)	2.030(3)	Ni(1) O(8)	2.006(3)
Ni(1) O(18)	2.084(3)	Ni(1) O(19)	2.090(4)
Ni(2) O(3)	2.018(3)	Ni(2) O(4)	1.999(3)
Ni(2) O(5)	1.989(3)	Ni(2) O(6)	2.011(3)
Ni(2) O(20)	2.118(3)	Ni(2) O(21)	2.069(3)
Ni₂Gd(7-C)			
Gd O(2)	2.454(3)	Gd O(2) ²⁾	2.454(3)
Gd O(3)	2.502(4)	Gd O(3) ²⁾	2.502(4)
Gd O(5)	2.432(4)	Gd O(5) ²⁾	2.432(4)
Gd O(8)	2.572(4)	Gd O(8) ²⁾	2.572(4)
Gd N(1)	2.674(3)	Gd N(1) ²⁾	2.674(3)
Ni O(1)	1.968(4)	Ni O(2)	1.987(3)
Ni O(3) ²⁾	2.009(4)	Ni O(4) ²⁾	1.970(4)
Ni O(10)	2.088(4)	Ni O(11)	2.106(4)
Ni₂Tb(8)			
Tb O(2)	2.447(3)	Tb O(2) ²⁾	2.447(3)
Tb O(3)	2.505(2)	Tb O(3) ²⁾	2.505(2)
Tb O(5)	2.418(3)	Tb O(5) ²⁾	2.418(3)
Tb O(8)	2.563(3)	Tb O(8) ²⁾	2.563(3)
Tb N(1)	2.662(3)	Tb N(1) ²⁾	2.662(3)
Ni O(1)	1.972(3)	Ni O(2)	2.006(2)
Ni O(3) ²⁾	2.018(3)	Ni O(4) ²⁾	1.980(3)
Ni O(10)	2.088(3)	Ni O(11)	2.105(3)
Ni₂Dy(9)			
Dy O(2)	2.438(2)	Dy O(2) ²⁾	2.438(2)
Dy O(3)	2.500(2)	Dy O(3) ²⁾	2.500(2)
Dy O(5)	2.412(2)	Dy O(5) ²⁾	2.412(2)
Dy O(8)	2.547(2)	Dy O(8) ²⁾	2.547(2)
Dy N(1)	2.657(3)	Dy N(1) ²⁾	2.657(3)
Ni O(1)	1.974(2)	Ni O(2)	2.004(2)
Ni O(3) ²⁾	2.013(2)	Ni O(4) ²⁾	1.977(2)
Ni O(10)	2.090(3)	Ni O(11)	2.100(3)
Ni₂Ho(10)			
Ho O(2)	2.429(4)	Ho O(3)	2.408(4)
Ho O(6)	2.410(4)	Ho O(7)	2.427(4)
Ho O(9)	2.450(4)	Ho O(10)	2.497(5)
Ho O(12)	2.457(4)	Ho O(13)	2.415(4)
Ho N(1)	2.596(5)	Ho N(2)	2.579(5)
Ni(1) O(1)	1.985(4)	Ni(1) O(2)	2.010(4)
Ni(1) O(7)	2.004(4)	Ni(1) O(8)	1.997(4)
Ni(1) O(18)	2.137(5)	Ni(1) O(19)	2.075(5)
Ni(2) O(3)	2.014(4)	Ni(2) O(4)	2.025(4)
Ni(2) O(5)	2.000(4)	Ni(2) O(6)	2.015(4)
Ni(2) O(20)	2.076(5)	Ni(2) O(21)	2.073(5)

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Ni₂Er(11)

Er	O(2)	2.396(3)	Er	O(3)	2.432(2)
Er	O(6)	2.423(3)	Er	O(7)	2.402(3)
Er	O(9)	2.491(3)	Er	O(10)	2.437(3)
Er	O(12)	2.406(3)	Er	O(13)	2.442(3)
Er	N(1)	2.586(3)	Er	N(2)	2.581(3)
Ni(1)	O(1)	2.013(3)	Ni(1)	O(2)	2.019(3)
Ni(1)	O(7)	2.020(3)	Ni(1)	O(8)	2.003(3)
Ni(1)	O(18)	2.079(3)	Ni(1)	O(19)	2.072(3)
Ni(2)	O(3)	2.007(3)	Ni(2)	O(4)	1.980(3)
Ni(2)	O(5)	1.995(3)	Ni(2)	O(6)	2.006(3)
Ni(2)	O(20)	2.132(3)	Ni(2)	O(21)	2.075(3)

Ni₂Tm(12)

Tm	O(2)	2.416(2)	Tm	O(3)	2.398(2)
Tm	O(6)	2.387(2)	Tm	O(7)	2.431(2)
Tm	O(9)	2.403(2)	Tm	O(10)	2.431(2)
Tm	O(12)	2.487(2)	Tm	O(13)	2.432(2)
Tm	N(1)	2.581(3)	Tm	N(2)	2.584(3)
Ni(1)	O(1)	1.996(2)	Ni(1)	O(2)	2.005(2)
Ni(1)	O(7)	2.015(2)	Ni(1)	O(8)	1.982(3)
Ni(1)	O(18)	2.078(2)	Ni(1)	O(19)	2.137(3)
Ni(2)	O(3)	2.022(2)	Ni(2)	O(4)	2.014(2)
Ni(2)	O(5)	2.011(2)	Ni(2)	O(6)	2.018(2)
Ni(2)	O(20)	2.072(3)	Ni(2)	O(21)	2.084(2)

Ni₂Yb(13)

Yb	O(2)	2.389(4)	Yb	O(3)	2.417(4)
Yb	O(6)	2.434(4)	Yb	O(7)	2.373(4)
Yb	O(9)	2.405(5)	Yb	O(10)	2.426(4)
Yb	O(12)	2.498(5)	Yb	O(13)	2.433(4)
Yb	N(1)	2.581(5)	Yb	N(2)	2.577(5)
Ni(1)	O(1)	2.012(4)	Ni(1)	O(2)	2.017(4)
Ni(1)	O(7)	2.027(4)	Ni(1)	O(8)	2.014(4)
Ni(1)	O(18)	2.078(5)	Ni(1)	O(19)	2.092(5)
Ni(2)	O(3)	2.009(4)	Ni(2)	O(4)	1.991(5)
Ni(2)	O(5)	1.993(4)	Ni(2)	O(6)	2.013(4)
Ni(2)	O(20)	2.082(4)	Ni(2)	O(21)	2.136(4)

Ni₂Lu(14)

Lu	O(2)	2.375(2)	Lu	O(3)	2.418(2)
Lu	O(6)	2.403(2)	Lu	O(7)	2.383(2)
Lu	O(9)	2.461(2)	Lu	O(10)	2.413(2)
Lu	O(12)	2.381(2)	Lu	O(13)	2.409(2)
Lu	N(1)	2.574(2)	Lu	N(2)	2.568(2)
Ni(1)	O(1)	2.007(2)	Ni(1)	O(2)	2.022(2)
Ni(1)	O(7)	2.015(2)	Ni(1)	O(8)	2.009(2)
Ni(1)	O(18)	2.083(2)	Ni(1)	O(19)	2.074(3)
Ni(2)	O(3)	2.006(2)	Ni(2)	O(4)	1.984(2)
Ni(2)	O(5)	1.997(2)	Ni(2)	O(6)	2.001(2)
Ni(2)	O(20)	2.138(2)	Ni(2)	O(21)	2.077(2)

Symmetry operation: 1) $-x, -y, -z$; 2) $-x, y, -z+1/2$