Supporting Information for:

Unusual undecanuclear heterobimetallic Zn_4Ln_7 (Ln = Gd，Dy) nano-sized clusters encapsulating two peroxide anions through spontaneous intake of dioxygen

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Table S1. The bond valence sum (BVS) calculations on O sites.[1]

Oxygen atoms	BVS	Assigned protonation levels
O(25)	0.36	H_2O
O(26)	0.36	H_2O
O(27)	0.36	H_2O
O(28)	0.38	H_2O
O(29)	1.27	OH
O(30)	1.26	OH

O(31)	1.31	O_2^{2-}
O(32)	1.13	
O(33)	1.32	O_2^{2-}
O(34)	1.14	
O(35)	1.29	OH
O(36)	1.27	OH

Table S2. SHAPE[2] analysis of compounds **1** and **2**.

		HPBY (D_{6h})	CU (O_h)	SAPR (D_{4d})	TDD (D_{2d})	JGBF (D_{2d})	JETBPY (D_{3h})	JBTPR (C_{2v})	BTPR (C_{2v})	JSD (D_{2d})
	Gd(1)	12.423	13.856	7.844	**5.522**	12.204	26.445	6.954	6.007	**5.825**
	Gd(2)	14.204	8.340	2.597	**1.076**	13.437	27.889	2.439	2.282	3.903
	Gd(3)	13.783	9.728	**3.277**	4.719	14.765	24.675	5.192	**3.685**	7.740
1	Gd(4)	13.387	9.753	**3.448**	4.306	15.917	25.240	5.123	**3.813**	7.030
	Gd(5)	13.947	9.814	**3.422**	4.679	14.601	24.711	5.375	**3.843**	7.672
	Gd(6)	14.505	8.687	2.374	**1.116**	13.651	28.403	2.396	2.214	3.882
	Gd(7)	14.901	10.218	**3.270**	4.178	16.233	25.643	4.813	**3.528**	6.750
	Dy(1)	12.438	13.973	7.578	**5.292**	11.905	26.912	6.662	5.728	**5.622**
	Dy(2)	16.104	14.061	9.835	**8.739**	12.685	21.848	9.763	**8.404**	12.487
	Dy(3)	14.134	9.907	**3.120**	3.886	16.354	26.081	4.670	**3.509**	6.526
2	Dy(4)	13.912	9.477	**3.265**	4.652	14.234	25.039	5.041	**3.571**	7.560
	Dy(5)	13.787	9.780	**3.118**	3.943	16.251	25.558	4.882	**3.691**	6.681
	Dy(6)	14.518	8.850	2.235	**1.249**	13.373	28.144	2.268	2.200	3.985
	Dy(7)	13.934	9.618	**3.168**	4.464	14.495	24.594	4.999	**3.524**	7.573

Abbreviations: HPBY-Hexagonal bipyramid, CU-Cube, SAPR-Square antiprism, TDD-Triangular dodecahedron, JGBF-Johnson-Gyrobifastigium J26, JETBPY-Johnson elongated triangular

bipyramid J14, JBTPR-Johnson biaugmented trigonal prism J50, BTPR-Biaugmented trigonal prism, JSD-Snub diphenoid

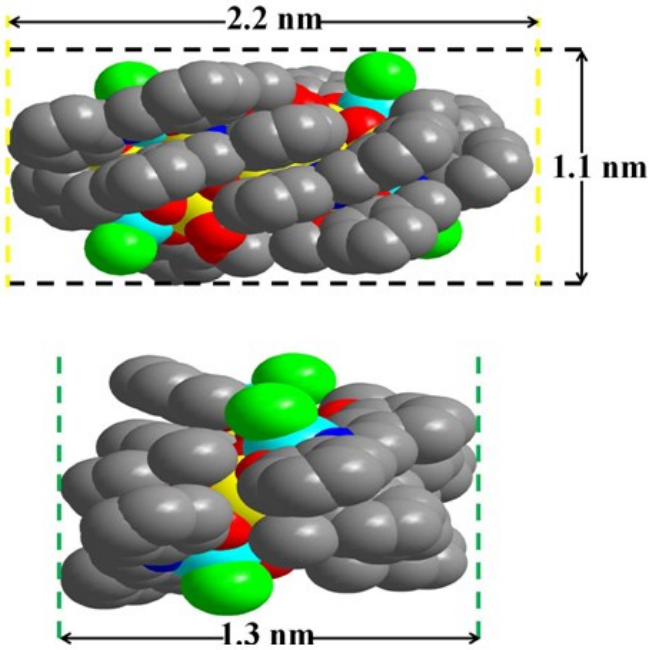

Fig. S1. Space-filling representations showing the dimensions and thickness of compound **2**. Color code: Dy, yellow; Zn, turquiose; O, red; N, blue; Cl, bright green.

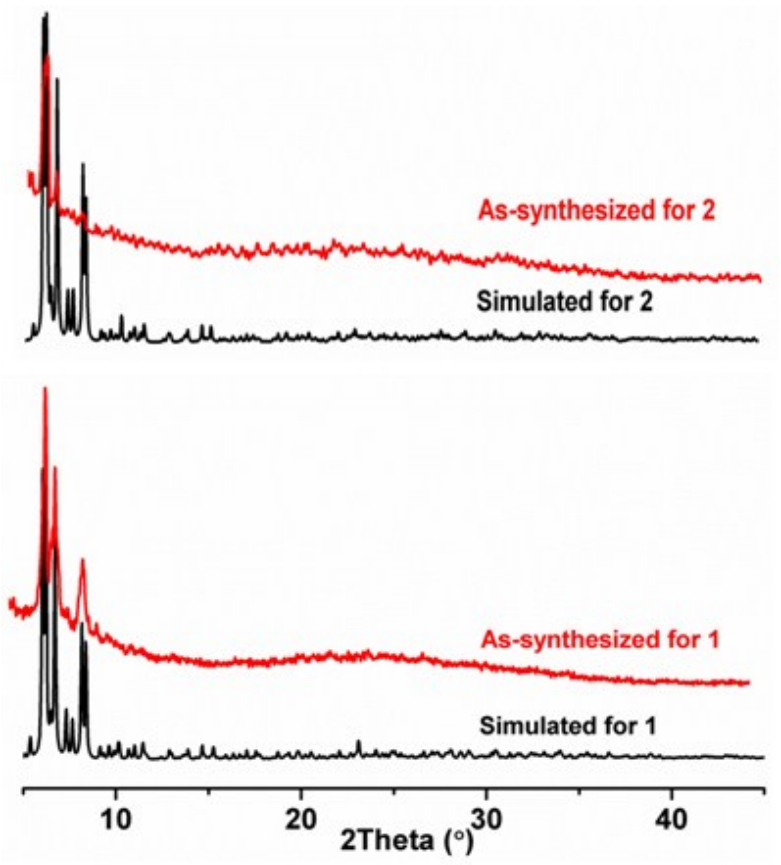

Fig. S2. Comparing the simulated PXRD (black) and experimetnal patterns of compounds **1** and **2**.

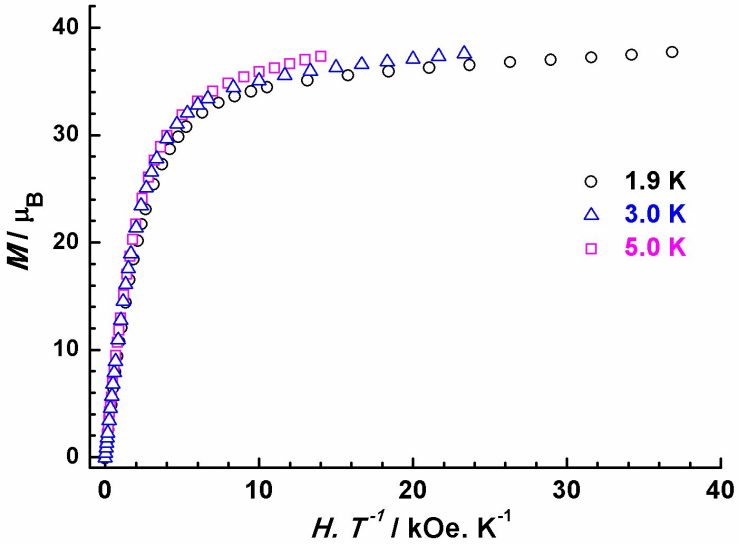

Fig. S3. Field dependence of the magnetization at low temperatures for **2**.

Table S3. χ_T, χ_S, τ and α values of **2** estimated by theoretical calculations on the basis of the generalized Debye model.[3]

T/K	1.9	2.2	2.5	3.0	3.5
χ_T/cm^3 mol^{-1}	41.19	37.19	32.77	28.98	24.39
χ_S/cm^3 mol^{-1}	11.80	10.81	9.22	9.02	7.60
τ/μsec	142	141	143	137	132
α	0.33	0.32	0.31	0.30	0.29
T/K	4.0	5.0	6.0	7.0	8.0
χ_T/cm^3 mol^{-1}	22.07	17.06	14.71	11.69	10.11
χ_S/cm^3 mol^{-1}	6.93	6.94	7.28	5.30	5.89
τ/μsec	107	106	79	41	33
α	0.29	0.27	0.27	0.31	0.30

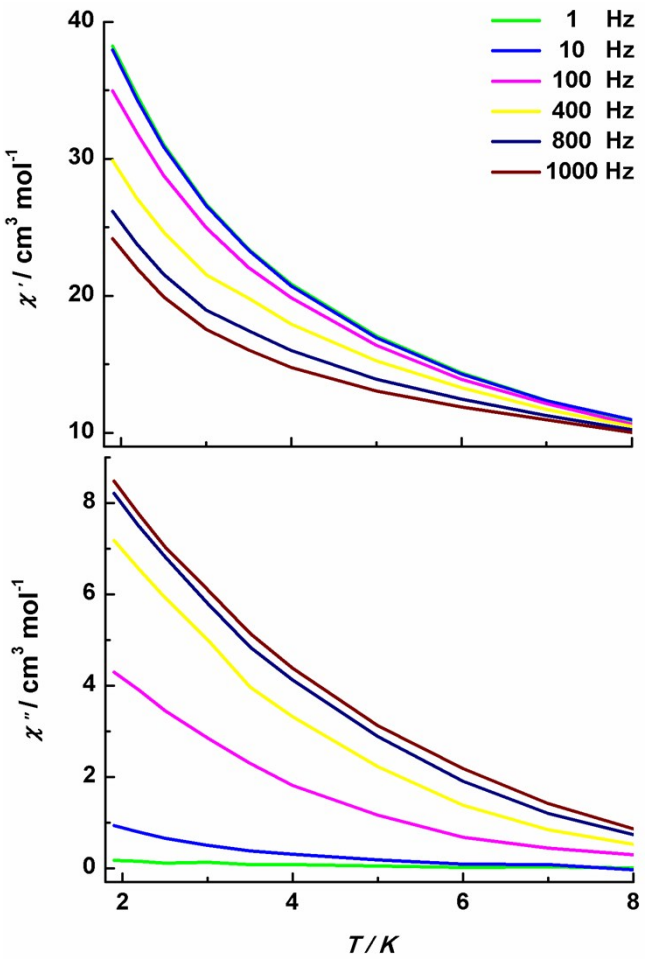

Fig. S4. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') components of the ac susceptibility (H_{dc} = 0 Oe and H_{ac} = 3 Oe) for **2**.

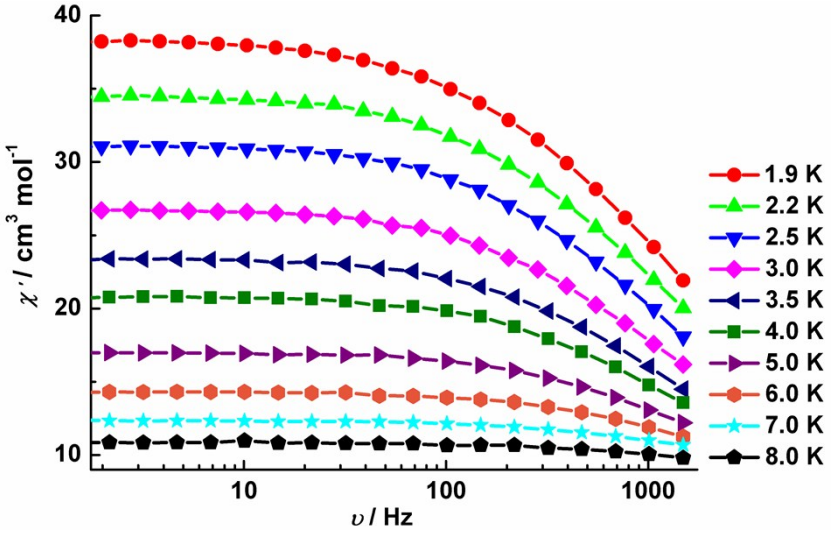

Fig. S5. Frequency dependence of the in-phase (χ') component of the ac magnetic susceptibility for **2** under zero applied dc field. Solid curves represent theoretical calculations on the basis of the generalized Debye model.[3]

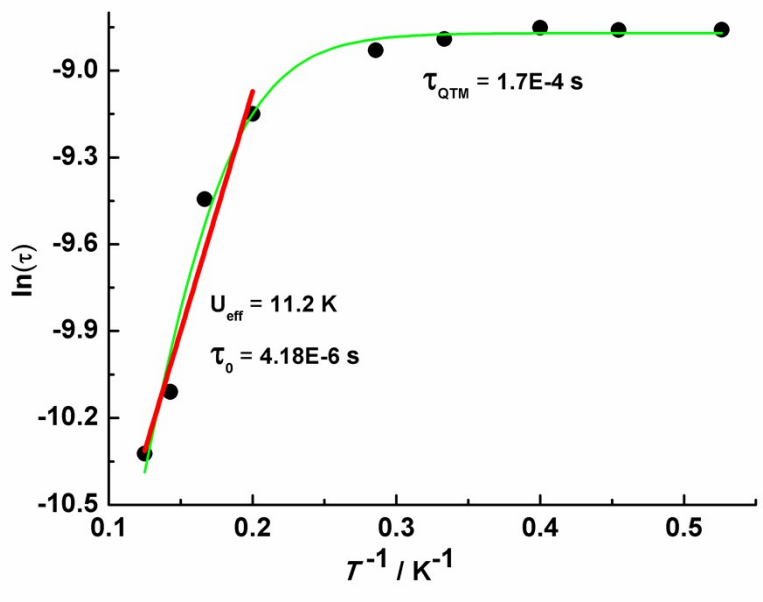

Fig. S6. Plot of inverse temperature versus the natural log of the relaxation time for **2** and the red line corresponds to a fit to the Arrhenius expression.

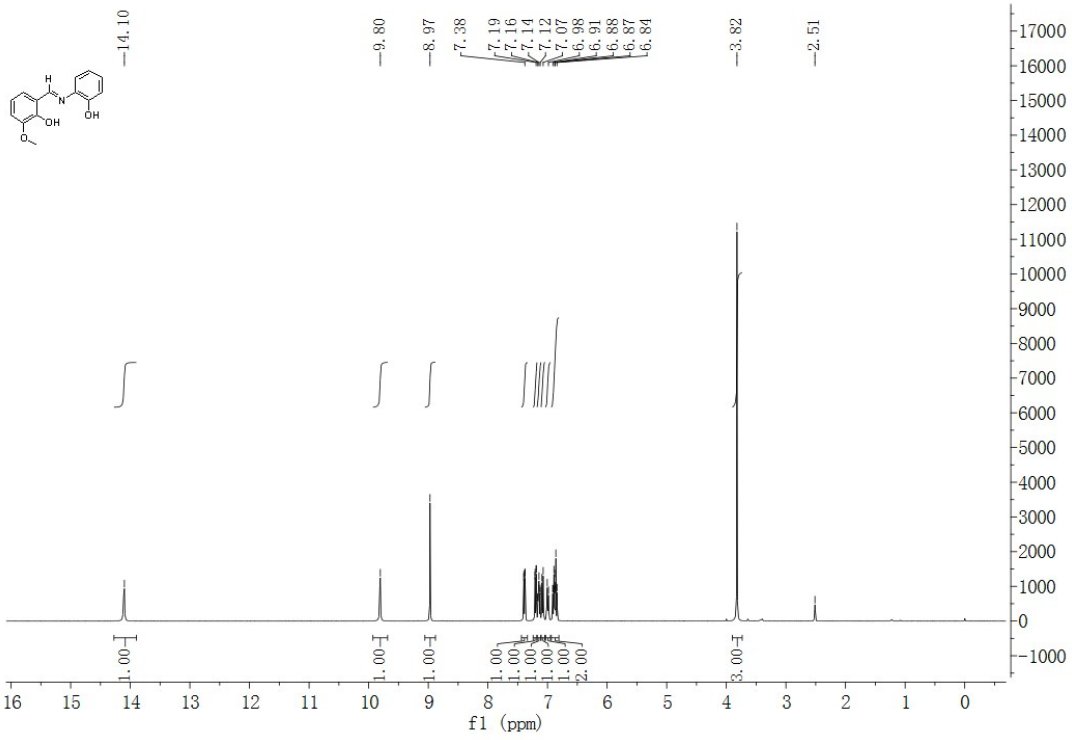

Fig. S7. ^{1}H NMR spectra of ligand H_2L at 298 K.

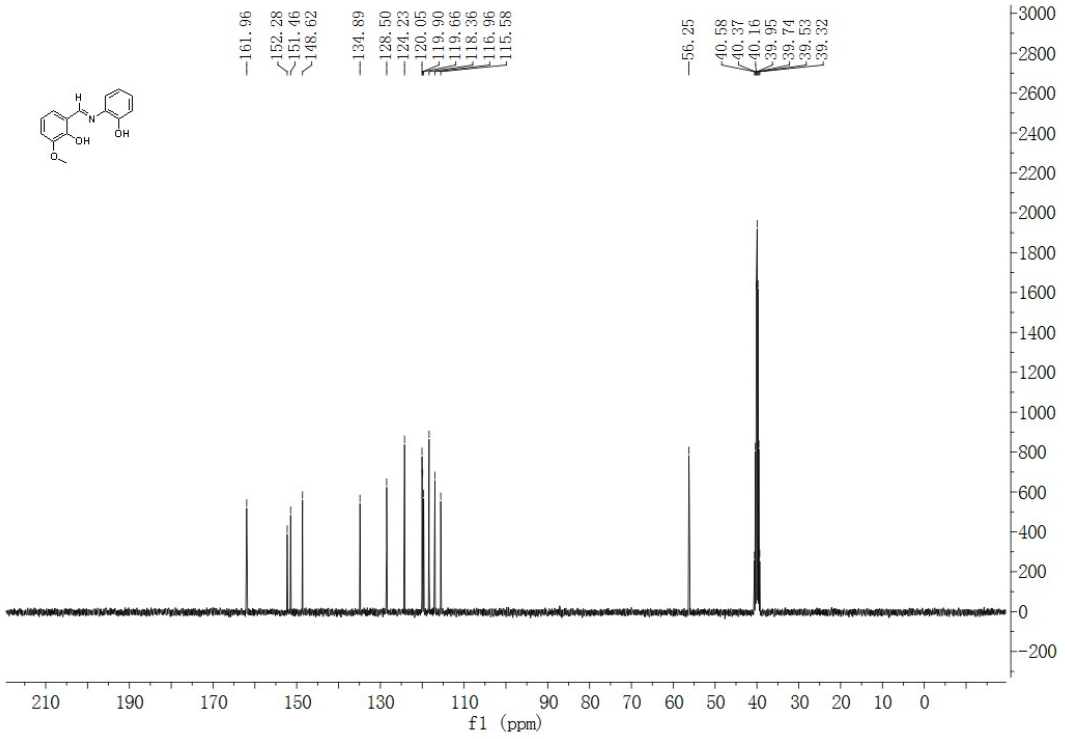

Fig. S8. $^{13}C\{^{1}H\}$ NMR spectra of ligand H_2L at 298 K.

Table S4. Crystallographic data and refinement parameters for compounds **1** and **2**.

Compound	**1**	**2**
formula	$C_{120}H_{120}N_{12}O_{40}Cl_5Zn_4Gd_7$	$C_{120}H_{120}N_{12}O_{40}Cl_5Zn_4Dy_7$
Mr (g/mol)	3909.75	3946.50
cryst syst	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
a/Å	16.0223(13)	16.2712(8)
b/Å	19.4348(14)	16.3688(9)
c/Å	27.978(2)	27.8061(13)
α/°	71.9570(10)	72.1550(10)
β/°	75.9180(10)	75.1570(10)
γ/°	66.9010(10)	66.4450(10)
V/Å^3]	7545.4(10)	7556.2(6)
T/K	177	177
Z	2	2
ρ_{calcd}/(g cm^{-3})	1.721	1.735
μ(Mo-Kα)/(mm^{-1})	3.815	4.198
F(000)	3794	3822
Data collected	41093	38618
Unique data	28920	26314
R_{int}	0.0436	0.0345
R_1 [I > 2σ(I)]	0.0592	0.0563
R_1 (all data)	0.1047	0.1689
ωR [I > 2σ(I)]	0.1376	0.0768
ωR_2 (all data)	0.1516	0.1807
GOF S	0.992	1.034

Table S5. Selected bond lengths (Å) and angles (°) for compounds **1** and **2**.

1		**2**	
Bond lengths (Å)			
Zn(1)-N(1)	2.055(7)	Zn(1)-N(1)	2.066(9)
Zn(1)-Cl(2)	2.245(3)	Zn(1)-Cl(2)	2.230(3)
Zn(1)-O(2)	2.011(6)	Zn(1)-O(2)	2.035(7)
Zn(1)-O(3)	2.118(7)	Zn(1)-O(3)	2.093(7)
Zn(1)-O(30)	2.082(7)	Zn(1)-O(30)	2.051(7)
Zn(2)-N(3)	2.086(7)	Zn(2)-N(3)	2.031(9)
Zn(2)-Cl(1)	2.246(3)	Zn(2)-Cl(1)	2.242(3)
Zn(2)-O(8)	2.030(6)	Zn(2)-O(8)	2.011(7)
Zn(2)-O(9)	2.106(7)	Zn(2)-O(9)	2.136(8)
Zn(2)-O(29)	2.064(6)	Zn(2)-O(29)	2.095(7)
Zn(3)-N(6)	2.078(7)	Zn(3)-N(6)	2.055(9)
Zn(3)-Cl(3)	2.240(4)	Zn(3)-Cl(3)	2.239(3)
Zn(3)-O(17)	2.018(6)	Zn(3)-O(17)	2.025(7)
Zn(3)-O(18)	2.109(6)	Zn(3)-O(18)	2.115(7)
Zn(3)-O(36)	2.077(5)	Zn(3)-O(36)	2.083(7)
Zn(4)-N(5)	2.071(8)	Zn(4)-N(5)	2.050(9)
Zn(4)-Cl(4)	2.251(3)	Zn(4)-Cl(4)	2.247(3)
Zn(4)-O(14)	2.016(6)	Zn(4)-O(14)	2.025(7)
Zn(4)- O(15)	2.113(6)	Zn(4)- O(15)	2.128(7)
Zn(4)- O(35)	2.089(5)	Zn(4)- O(35)	2.071(6)
Gd(1)-O(6)	2.343(7)	Dy(1)-O(6)	2.323(7)
Gd(1)-O(12)	2.350(6)	Dy(1)-O(12)	2.331(7)
Gd(1)-O(21)	2.344(5)	Dy(1)-O(21)	2.324(7)
Gd(1)-O(24)	2.353(6)	Dy(1)-O(24)	2.316(7)
Gd(1)-O(31)	2.381(5)	Dy(1)-O(31)	2.358(6)
Gd(1)-O(32)	2.366(6)	Dy(1)-O(32)	2.345(7)
Gd(1)-O(33)	2.357(5)	Dy(1)-O(33)	2.336(7)
Gd(1)-O(34)	2.370(6)	Dy(1)-O(34)	2.334(6)
Gd(2)-O(3)	2.321(6)	Dy(2)-O(3)	2.289(7)
Gd(2)-O(4)	2.496(5)	Dy(2)-O(4)	2.486(7)
Gd(2)-O(5)	2.478(6)	Dy(2)-O(5)	2.403(6)
Gd(2)-O(9)	2.300(7)	Dy(2)-O(9)	2.290(7)
Gd(2)-O(10)	2.507(6)	Dy(2)-O(10)	2.478(7)
Gd(2)-O(11)	2.426(5)	Dy(2)-O(11)	2.447(6)
Gd(2)-O(29)	2.340(6)	Dy(2)-O(29)	2.296(7)
Gd(2)-O(30)	2.317(7)	Dy(2)-O(30)	2.330(7)
Gd(3)-N(2)	2.474(7)	Dy(3)-N(2)	2.414(8)
Gd(3)-O(5)	2.365(5)	Dy(3)-O(5)	2.340(7)
Gd(3)-O(6)	2.348(6)	Dy(3)-O(6)	2.337(7)
Gd(3)-O(8)	2.352(7)	Dy(3)-O(8)	2.316(7)
Gd(3)-O(25)	2.440(6)	Dy(3)-O(25)	2.414(8)

Gd(3)-O(29)	2.395(6)	Dy(3)-O(29)	2.352(6)
Gd(3)-O(31)	2.414(6)	Dy(3)-O(31)	2.290(7)
Gd(3)-O(32)	2.391(6)	Dy(3)-O(32)	2.501(7)
Gd(4)-N(7)	2.428(7)	Dy(4)-N(7)	2.451(9)
Gd(4)-O(17)	2.344(6)	Dy(4)-O(17)	2.311(6)
Gd(4)-O(20)	2.385(6)	Dy(4)-O(20)	2.343(7)
Gd(4)-O(21)	2.360(6)	Dy(4)-O(21)	2.342(7)
Gd(4)-O(26)	2.520(8)	Dy(4)-O(26)	2.412(8)
Gd(4)-O(33)	2.489(7)	Dy(4)-O(33)	2.372(6)
Gd(4)-O(34)	2.331(5)	Dy(4)-O(34)	2.346(7)
Gd(4)- O(36)	2.396(6)	Dy(4)-O(36)	2.365(7)
Gd(5)-N(8)	2.490(7)	Dy(5)-N(8)	2.406(9)
Gd(5)-O(14)	2.356(6)	Dy(5)-O(14)	2.294(7)
Gd(5)-O(23)	2.390(6)	Dy(5)-O(23)	2.349(6)
Gd(5)-O(24)	2.358(6)	Dy(5)-O(24)	2.311(7)
Gd(5)-O(27)	2.423(7)	Dy(5)-O(27)	2.411(8)
Gd(5)-O(33)	2.362(5)	Dy(5)-O(33)	2.308(6)
Gd(5)-O(34)	2.419(6)	Dy(5)-O(34)	2.465(7)
Gd(5)-O(35)	2.400(5)	Dy(5)-O(35)	2.352(6)
Gd(6)-O(15)	2.322(6)	Dy(6)-O(15)	2.290(7)
Gd(6)-O(18)	2.338(6)	Dy(6)-O(18)	2.301(6)
Gd(6)-O(19)	2.498(6)	Dy(6)-O(19)	2.487(7)
Gd(6)-O(20)	2.424(6)	Dy(6)-O(20)	2.427(6)
Gd(6)-O(22)	2.498(6)	Dy(6)-O(22)	2.478(7)
Gd(6)-O(23)	2.446(5)	Dy(6)-O(23)	2.411(7)
Gd(6)-O(35)	2.332(7)	Dy(6)-O(35)	2.297(7)
Gd(6)-O(36)	2.319(6)	Dy(6)-O(36)	2.292(7)
Gd(7)-N(4)	2.448(7)	Dy(7)-N(4)	2.437(8)
Gd(7)-O(2)	2.347(6)	Dy(7)-O(2)	2.324(7)
Gd(7)-O(11)	2.370(6)	Dy(7)-O(11)	2.334(6)
Gd(7)-O(12)	2.363(6)	Dy(7)-O(12)	2.327(7)
Gd(7)-O(28)	2.471(7)	Dy(7)-O(28)	2.391(7)
Gd(7)-O(30)	2.399(6)	Dy(7)-O(30)	2.359(6)
Gd(7)-O(31)	2.333(6)	Dy(7)-O(31)	2.388(7)
Gd(7)-O(32)	2.490(7)	Dy(7)-O(32)	2.343(7)
Gd(1)···Gd(3)	3.6652(7)	Dy(1)···Dy(3)	3.6152(10)
Gd(1)···Gd(4)	3.6524(7)	Dy(1)···Dy(4)	3.6356(9)
Gd(1)···Gd(5)	3.6703(7)	Dy(1)···Dy(5)	3.6036(6)
Gd(1)···Gd(7)	3.6659(7)	Dy(1)···Dy(7)	3.6286(6)
Gd(2)···Gd(3)	3.8348(10)	Dy(2)···Dy(3)	3.7511(7)
Gd(2)···Gd(7)	3.7978(7)	Dy(2)···Dy(7)	3.799(1)
Gd(3)···Gd(7)	4.3401(9)	Dy(3)···Dy(7)	4.2800(7)
Gd(4)···Gd(5)	4.3313(9)	Dy(4)···Dy(5)	4.2606(8)
Gd(4)···Gd(6)	3.8024(10)	Dy(4)···Dy(6)	3.7962(6)

Gd(5)···Gd(6)	3.8255(7)	Dy(5)···Dy(6)	3.7600(9)
O(31)···O(32)	1.526(7)	O(31)···O(32)	1.539(9)
O(33)···O(34)	1.502(9)	O(33)···O(34)	1.514(9)
	Bond angles (°)		
Gd(1)-O(6)-Gd(3)	102.7(2)	Dy(1)-O(6)-Dy(3)	101.8(3)
Gd(1)-O(31)-Gd(3)	99.7(2)	Dy(1)-O(31)-Dy(3)	102.1(3)
Gd(1)-O(32)-Gd(3)	100.8(2)	Dy(1)-O(32)-Dy(3)	96.4(3)
Gd(1)-O(21)-Gd(4)	101.9(2)	Dy(1)-O(21)-Dy(4)	102.4(3)
Gd(1)-O(33)-Gd(4)	97.8(2)	Dy(1)-O(33)-Dy(4)	101.1(3)
Gd(1)-O(34)-Gd(4)	102.0 (2)	Dy(1)-O(34)-Dy(4)	102.0(3)
Gd(1)-O(24)-Gd(5)	102.4(2)	Dy(1)-O(24)-Dy(5)	102.3(2)
Gd(1)-O(33)-Gd(5)	102.1 (2)	Dy(1)-O(33)-Dy(5)	101.8(2)
Gd(1)-O(34)-Gd(5)	100.1(2)	Dy(1)-O(34)-Dy(5)	97.3(2)
Gd(1)-O(12)-Gd(7)	102.1 (2)	Dy(1)-O(12)-Dy(7)	102.3(3)
Gd(1)-O(31)-Gd(7)	102.1(2)	Dy(1)-O(31)-Dy(7)	99.7(3)
Gd(1)-O(32)-Gd(7)	98.0(2)	Dy(1)-O(32)-Dy(7)	101.4(2)
Gd(2)-O(5)-Gd(3)	104.7(19)	Dy(2)-O(5)-Dy(3)	104.5(2)
Gd(2)-O(29)-Gd(3)	108.2(2)	Dy(2)-O(29)-Dy(3)	107.6(3)
Gd(2)-O(11)-Gd(7)	104.69(19)	Dy(2)-O(11)-Dy(7)	105.2(2)
Gd(2)-O(30)-Gd(7)	107.3(2)	Dy(2)-O(30)-Dy(7)	108.2(3)
Gd(3)-O(31)-Gd(7)	132.2 (2)	Dy(3)-O(31)-Dy(7)	132.4(3)
Gd(3)-O(32)-Gd(7)	125.5(2)	Dy(3)-O(32)-Dy(7)	124.1(3)
Gd(4)-O(33)-Gd(5)	126.5(3)	Dy(4)-O(33)-Dy(5)	131.1(3)
Gd(4)-O(34)-Gd(5)	131.5(3)	Dy(4)-O(34)-Dy(5)	124.6(3)
Gd(4)-O(20)-Gd(6)	104.5(2)	Dy(4)-O(20)-Dy(6)	105.5(3)
Gd(4)-O(36)-Gd(6)	107.5(3)	Dy(4)-O(36)-Dy(6)	109.2(3)
Gd(5)-O(23)-Gd(6)	104.6(2)	Dy(5)-O(23)-Dy(6)	104.3(2)
Gd(5)-O(35)-Gd(6)	107.9(3)	Dy(5)-O(35)-Dy(6)	107.7(3)

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