Electronic Supplementary Information

Coordination Control of a Semicarbazide Schiff Base Ligand for Spontaneous Aggregation of a Ni_2Ln_2 Cubane Family: Influence of Ligand Arms and Carboxylate Bridges on the Organization of the Magnetic Core

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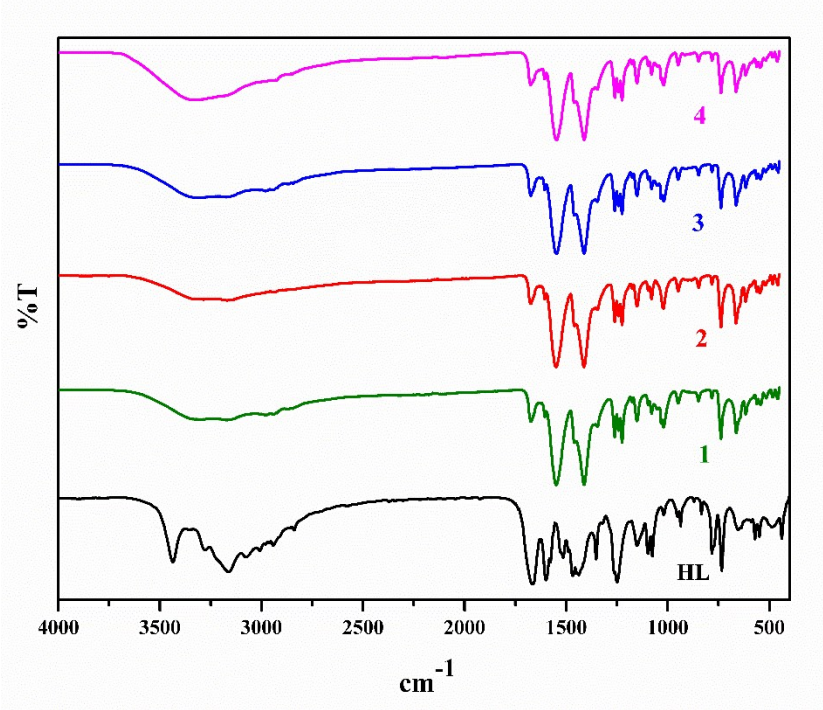


Figure S1. FT-IR spectra of complexes **1-4**

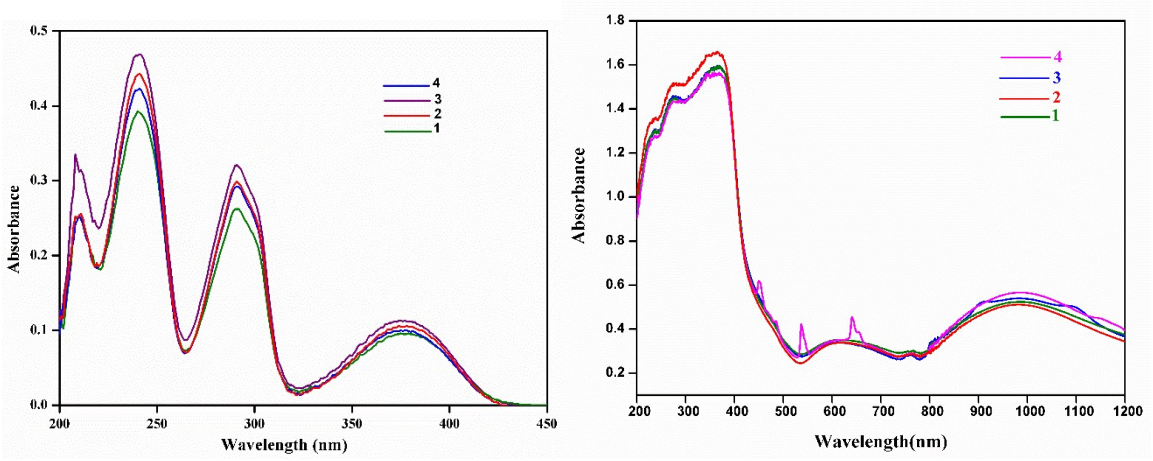


Figure S2. UV-Vis spectra of complexes **1-4** in solution (left) and in solid state (right)

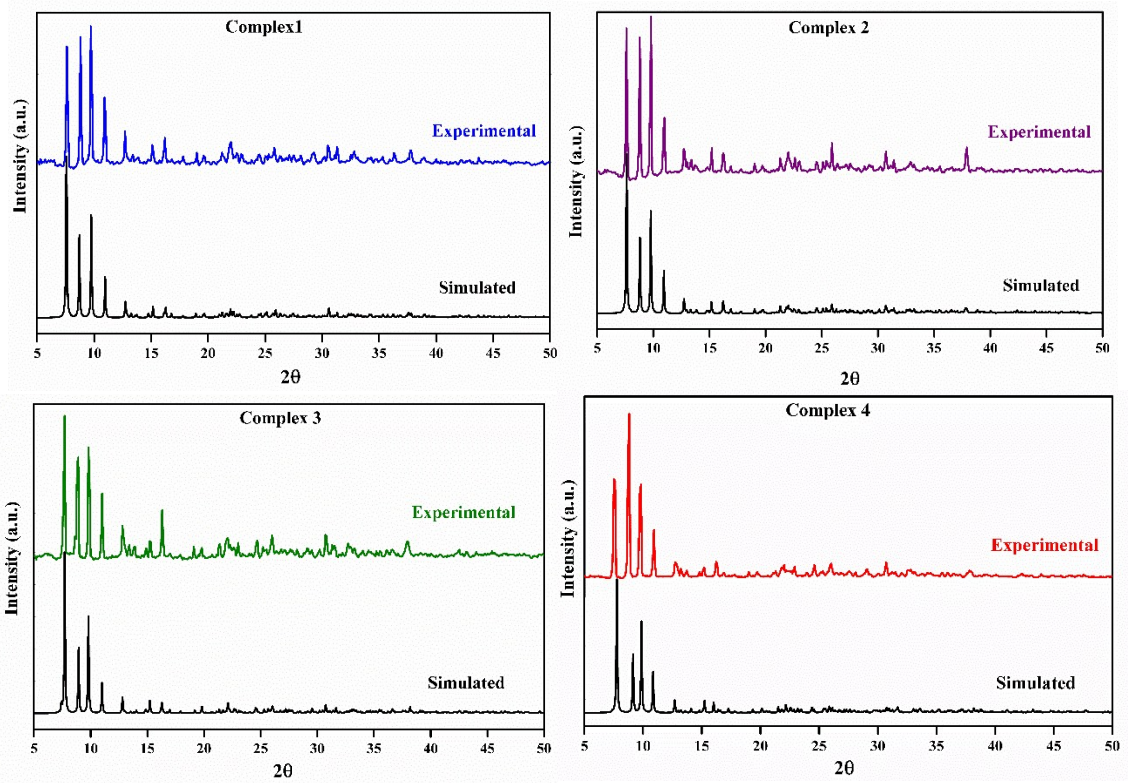


Figure S3. Simulated and experimental powder XRD patterns of complexes **1-4**

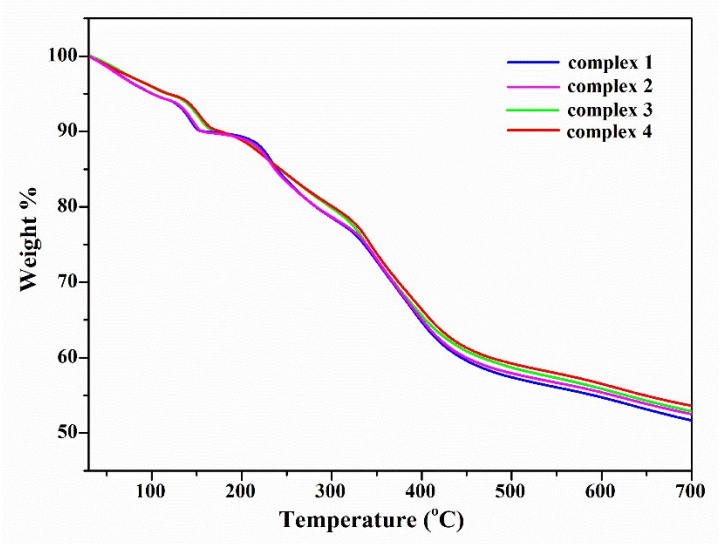
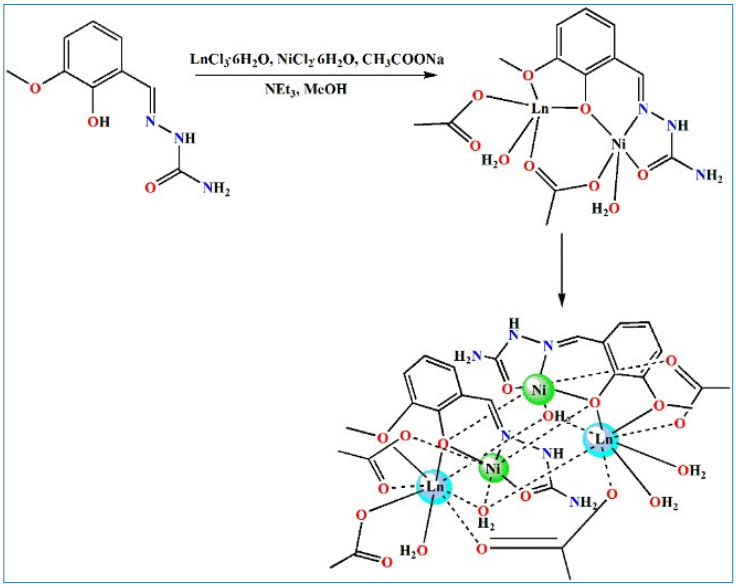
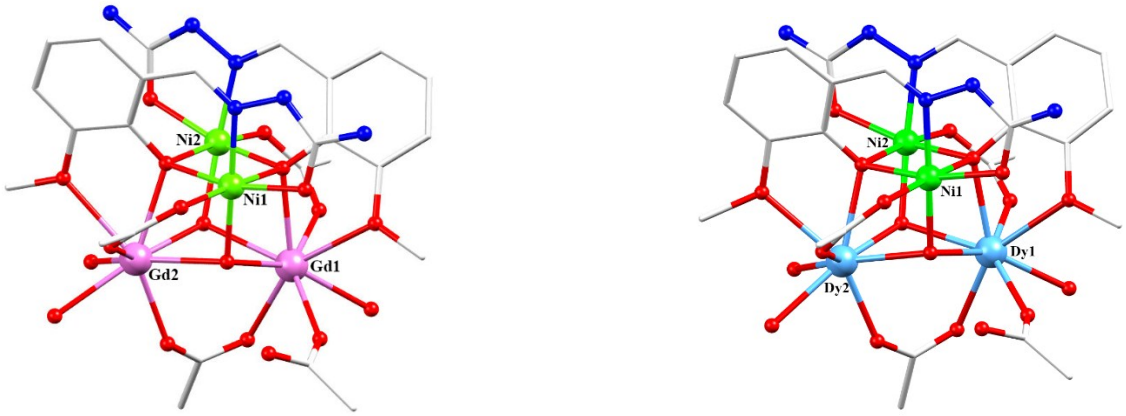


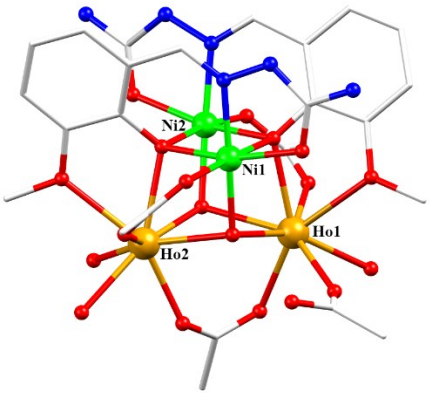
Figure S4. Thermogravimetric (TG) analysis of complexes **1**-**4**. The % of weight loss in 40-125℃ is 5.8, 4.4, 5.3, 5.4 for complexes **1-4** respectively.



Scheme S1 Most probable aggregation route



(a) (b)



(c)

Figure S5. Molecular structure of complex **1**(a)**, 3**(b) and **4**(c)

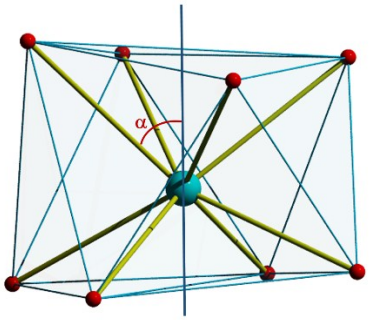


Figure S6. The angle α, half of the angle between the opposite ligands within a hemisphere

Table S1. Selected bond lengths (Å) and bond angles (˚) for complexes **1-4**

Bond lengths (Å)				
	1 (Gd)	**2** (Tb)	**3** (Dy)	**4** (Ho)
Ln1–O2	2.465(6)	2.474(5)	2.419(8)	2.442(3)
Ln1– O3	2.361(7)	2.341(6)	2.312(8)	2.330(4)
Ln1–O4	2.394(7)	2.411(7)	2.374(9)	2.428(4)
Ln1–O5	2.530(9)	2.556(7)	2.520(10)	2.561(4)
Ln1–O7	2.337(7)	2.340(6)	2.318(9)	2.337(4)
Ln1–O11	2.371(9)	2.367(7)	2.331(9)	2.340(4)
Ln1–O13	2.342(8)	2.317(6)	2.309(8)	2.297(4)
Ln1–O17	2.410(7)	2.405(7)	2.393(9)	2.397(4)
Ni1–N1	1.997(9)	2.017(7)	1.996(10)	2.022(5)
Ni1–O1	2.035(8)	2.059(6)	2.033(8)	2.065(4)
Ni1–O2	2.231(6)	2.230(5)	2.198(8)	2.250(3)
Ni1–O3	2.003(7)	2.012(6)	1.989(8)	2.022(3)
Ni1–O10	2.048(7)	2.050(6)	2.037(9)	2.060(4)

Ni1–O15	2.067(9)	2.072(7)	2.058(9)	2.068(4)
Ln2–O1	2.467(8)	2.486(6)	2.453(8)	2.442(4)
Ln2–O3	2.357(8)	2.366(6)	2.317(9)	2.346(4)
Ln2–O4	2.388(7)	2.384(7)	2.330(11)	2.342(4)
Ln2–O6	2.595(11)	2.620(9)	2.554(12)	2.561(5)
Ln2–O9	2.332(9)	2.320(8)	2.291(11)	2.317(4)
Ln2–O12	2.344(9)	2.351(8)	2.293(10)	2.314(4)
Ln2–O18	2.389(11)	2.392(9)	2.376(12)	2.372(4)
Ln2–O19	2.436(11)	2.437(10)	2.415(14)	2.437(5)
Ni2–N4	1.998(10)	2.024(7)	1.978(11)	2.032(5)
Ni2–O1	2.237(7)	2.227(6)	2.203(8)	2.228(4)
Ni2–O2	2.030(7)	2.050(6)	2.016(8)	2.069(3)
Ni2–O4	2.000(8)	2.011(6)	1.984(9)	2.020(4)
Ni2–O8	2.064(7)	2.059(6)	2.074(9)	2.083(4)
Ni2–O16	2.083(8)	2.089(7)	2.072(9)	2.107(4)
Ln1–Ln2	3.786	3.779	3.737	3.772
Ln1–Ni1	3.541	3.538	3.475	3.492
Ln1–Ni2	3.423	3.440	3.390	3.443
Ln2–Ni1	3.384	3.396	3.355	3.377
Ln2–Ni2	3.593	3.598	3.544	3.567
Ni1–Ni2	3.209	3.225	3.181	3.255

Bond angles (°)				
	(**1**) Gd	(**2**) Tb	(**3**) Dy	(**4**) Ho
Ni1–O1–Ni2	97.3(3)	97.5(2)	97.3(3)	98.54(15)
Ni1–O1–Ln2	97.0(3)	96.2(2)	96.4(3)	96.71(14)
Ni2–O1–Ln2	99.5(3)	99.3(2)	99.0(3)	99.49(13)
Ni1–O2–Ni2	97.6(3)	97.7(2)	98.0(3)	97.72(14)
Ni1–O2– Ln1	97.8(2)	97.4(2)	97.6(3)	96.94(13)
Ni2–O2– Ln1	98.8(3)	98.6(2)	99.3(3)	99.15(13)
Ni1–O3– Ln1	108.2(3)	108.5(2)	107.6(3)	107.55(15)
Ni1–O3– Ln2	101.5(3)	101.4(2)	102.1(3)	100.99(15)
Ln1–O3– Ln2	106.7(3)	106.8(2)	107.7(3)	107.55(13)
Ni2–O4– Ln1	102.0(3)	101.8(3)	101.8(4)	101.06(15)
Ni2–O4– Ln2	109.6(3)	109.6(3)	110.2(4)	109.50(16)
Ln1–O4– Ln2	104.7(3)	104.0(2)	105.2(3)	104.51(13)

Table S2. Continuous Shape Measures Analysis for all Lanthanide ions. List of reference shapes and abbreviations. Bold is for the lowest value for each metal center

*Structure [ML_8]	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8	JSD-8	TT-8	ETBPY-8
Complex1 Gd1	31.475	23.355	16.134	10.479	2.415	**0.623**	13.801	30.013	2.602	2.114	2.976	11.321	25.679
Complex1 Gd2	28.023	23.070	17.265	11.103	**0.737**	2.332	15.010	26.736	2.333	1.353	4.668	11.912	22.003
Complex2 Tb1	31.453	23.160	16.067	10.516	2.397	**0.650**	13.751	30.007	2.569	2.069	3.023	11.334	25.670
Complex2 Tb2	28.486	22.433	16.776	10.762	**0.755**	2.424	14.914	26.370	2.421	1.533	4.761	11.549	21.720
Complex3 Dy1	31.261	23.125	16.187	10.533	2.267	**0.674**	13.539	30.020	2.482	1.972	3.017	11.381	25.184
Complex3 Dy2	28.520	22.506	17.349	11.097	**0.684**	2.450	15.393	26.144	2.632	1.765	4.915	11.857	21.490
Complex4 Ho1	31.882	22.617	16.343	10.549	2.246	**0.722**	13.429	29.941	2.362	1.899	3.151	11.347	25.410
Complex4 Ho2	29.132	22.137	16.492	10.483	**0.698**	2.437	14.865	26.490	2.492	1.781	4.792	11.283	21.639

*OP-8	D_{8h}	Octagon
HPY-8	C_{7v}	Heptagonal pyramid
HBPY-8	D_{6h}	Hexagonal bipyramid
CU-8	O_h	Cube
SAPR-8	D_{4d}	Square antiprism
TDD-8	D_{2d}	Triangular dodecahedron
JGBF-8	D_{2d}	Johnson gyrobifastigium J26
JETBPY-8	D_{3h}	Johnson elongated triangular bipyramid J14
JBTPR-8	C_{2v}	Biaugmented trigonal prism J50
BTPR-8	C_{2v}	Biaugmented trigonal prism
JSD-8	D_{2d}	Snub diphenoid J84
TT-8	T_d	Triakis tetrahedron
ETBPY-8	D_{3h}	Elongated trigonal bipyramid

Table S3. The overview of the structural and magnetic parameters for some Ni_2-Ln_2 cube complexes

CSD code	*J* values (cm^{-1})	Angles	Remarks	Reference No.
OTEXUH	*J*(Ni-Ni) = −3.638 *J*(Ni-Gd) = 0.919 *J*(Gd-Gd) = assumed as '0'	<Ni-O-Ni = 99.72°, 98.44° <Gd-O-Gd = 108.77°, 109.36°	Ni_2Dy_2 complex displays slow relaxation of magnetization	52
WAMXIT	*J*(Ni-Ni) = +3.28 *J*(Ni-Gd) = +0.46 *J*(Gd-Gd) = −0.19	<Ni–O–Ni = 96.65°, 98.56° <Gd-O-Gd = 102.66°, 104.27°	The Ni_2Dy_2 complex does not behave as a SMM	57
REWXIC	*J*(Ni-Ni) = +3.30 *J*(Ni-Gd) = +0.26 *J*(Gd-Gd) = −0.11	<Ni–O–Ni = 98.06° <Gd-O-Gd = 109.62°	Out-of-phase signals in ac susceptibilities above 1.9 K was not observed	58

DIJFOU	J(Ni-Ni) = +5.20 J(Ni-Gd) = +0.86 J(Gd-Gd) = −0.0034	<Ni–O–Ni = 98.63°, 98.13° <Gd-O-Gd = 108.14˚, 109.04˚	Ni_4Dy_4 Complex is not SMM	59
Complex-**1**	J(Ni-Ni) = −0.91 J(Ni-Gd) = +0.02 J(Gd-Gd) = +0.14	<Ni–O–Ni = 97.46°, 97.67° <Gd-O-Gd = 104.48˚, 106.91˚	Out-of-phase ac susceptibility signals absent	This work