

Heterometallic Cu-Ln complexes: Synthesis, crystal structures and magnetic characterization

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Table S1 Selected bond lengths [Å] and angles [°] for complex **1**

Complex 1					
Ho(1)-O(2)	2.319(11)	Ho(1)-O(6)	2.419(16)	Cu(1)-O(1)	1.930(11)
Ho(1)-O(1)	2.343(11)	Ho(1)-O(8)	2.391(13)	Cu(1)-O(2)	1.931(11)
Ho(1)-O(3)	2.587(12)	Ho(1)-O(9)	2.304(15)	Cu(1)-N(1)	1.910(15)
Ho(1)-O(4)	2.548(11)	Cu(1)-Cl(1)	2.784(6)	Cu(1)-N(2)	1.941(14)
Ho(1)-O(5)	2.412(14)	Ho(1)-Cu(1)	3.381(2)	O(6)-Ho(1)-O(3)	115.5(4)
Ho(1)-N(4)	2.414(16)	O(1)-Ho(1)-O(6)	145.9(5)	O(4)-Ho(1)-O(3)	156.3(4)
Ho(1)-N(3)	2.905(16)	O(9)-Ho(1)-O(6)	136.0(4)	O(2)-Ho(1)-N(3)	133.8(5)
O(2)-Ho(1)-O(1)	67.0(4)	O(8)-Ho(1)-O(6)	71.9(5)	O(1)-Ho(1)-N(3)	129.1(5)
O(2)-Ho(1)-O(9)	77.0(5)	O(5)-Ho(1)-O(6)	52.2(4)	O(9)-Ho(1)-N(3)	142.4(4)
O(1)-Ho(1)-O(9)	78.0(5)	N(4)-Ho(1)-O(6)	72.1(5)	O(8)-Ho(1)-N(3)	71.2(5)
O(2)-Ho(1)-O(8)	73.0(5)	O(2)-Ho(1)-O(4)	62.5(4)	O(5)-Ho(1)-N(3)	26.7(4)
O(1)-Ho(1)-O(8)	76.6(5)	O(1)-Ho(1)-O(4)	128.7(4)	N(4)-Ho(1)-N(3)	71.2(5)
O(9)-Ho(1)-O(8)	146.4(5)	O(9)-Ho(1)-O(4)	82.3(5)	O(6)-Ho(1)-N(3)	25.5(4)
O(2)-Ho(1)-O(5)	146.7(5)	O(8)-Ho(1)-O(4)	96.8(5)	O(4)-Ho(1)-N(3)	93.8(5)
O(1)-Ho(1)-O(5)	106.7(5)	O(5)-Ho(1)-O(4)	120.2(5)	O(3)-Ho(1)-N(3)	90.9(5)
O(9)-Ho(1)-O(5)	135.3(5)	N(4)-Ho(1)-O(4)	80.9(5)	N(1)-Cu(1)-O(1)	94.3(6)
O(8)-Ho(1)-O(5)	73.7(5)	O(6)-Ho(1)-O(4)	68.6(4)	O(2)-Cu(1)-O(1)	83.6(5)
O(2)-Ho(1)-N(4)	134.1(5)	O(2)-Ho(1)-O(3)	127.2(4)	N(2)-Cu(1)-O(1)	166.0(7)
O(1)-Ho(1)-N(4)	133.6(5)	O(1)-Ho(1)-O(3)	62.0(4)	N(1)-Cu(1)-Cl(1)	86.6(5)
O(9)-Ho(1)-N(4)	71.3(6)	O(9)-Ho(1)-O(3)	79.8(5)	O(2)-Cu(1)-Cl(1)	97.2(4)
O(8)-Ho(1)-N(4)	142.1(6)	O(8)-Ho(1)-O(3)	106.7(5)	N(2)-Cu(1)-Cl(1)	98.7(5)
O(5)-Ho(1)-N(4)	75.0(5)	O(5)-Ho(1)-O(3)	65.4(5)	O(1)-Cu(1)-Cl(1)	95.3(4)
O(2)-Ho(1)-O(6)	114.1(5)	N(4)-Ho(1)-O(3)	78.7(5)	N(1)-Cu(1)-Ho(1)	136.5(5)

Table S2 Selected bond lengths [Å] and angles [°] for complex **2**

Complex 2					
Gd(1)-O(1)	2.370(10)	Gd(1)-O(6)	2.518(11)	Cu(1)-O(1)	1.939(10)
Gd(1)-O(2)	2.368(10)	Gd(1)-O(8)	2.431(11)	Cu(1)-O(2)	1.925(11)
Gd(1)-O(3)	2.645(10)	Gd(1)-O(9)	2.364(10)	Cu(1)-N(1)	1.915(15)
Gd(1)-O(4)	2.587(10)	Gd(1)-N(4)	2.478(14)	Cu(1)-N(2)	1.963(14)
Gd(1)-O(5)	2.486(10)	Cu(1)-Cl(1)	2.761(4)	Gd(1)···Cu(1)	3.431(2)
O(1)-Gd(1)-O(9)	78.6(4)	O(8)-Gd(1)-O(6)	71.4(4)	O(1)-Gd(1)-N(3)	129.3(4)
O(1)-Gd(1)-O(2)	65.7(3)	O(5)-Gd(1)-O(6)	50.8(4)	O(9)-Gd(1)-N(3)	141.9(4)
O(9)-Gd(1)-O(2)	76.2(4)	N(4)-Gd(1)-O(6)	70.9(4)	O(2)-Gd(1)-N(3)	135.1(4)
O(1)-Gd(1)-O(8)	76.3(4)	O(1)-Gd(1)-O(4)	127.9(3)	O(8)-Gd(1)-N(3)	71.1(4)
O(9)-Gd(1)-O(8)	146.9(4)	O(9)-Gd(1)-O(4)	82.2(4)	O(5)-Gd(1)-N(3)	25.7(4)
O(2)-Gd(1)-O(8)	74.0(4)	O(2)-Gd(1)-O(4)	62.8(3)	N(4)-Gd(1)-N(3)	69.5(4)
O(1)-Gd(1)-O(5)	107.5(4)	O(8)-Gd(1)-O(4)	96.7(4)	O(6)-Gd(1)-N(3)	25.2(4)
O(9)-Gd(1)-O(5)	136.1(4)	O(5)-Gd(1)-O(4)	119.6(4)	O(4)-Gd(1)-N(3)	94.1(4)
O(2)-Gd(1)-O(5)	146.8(4)	N(4)-Gd(1)-O(4)	81.1(4)	O(3)-Gd(1)-N(3)	91.0(4)
O(8)-Gd(1)-O(5)	72.8(4)	O(6)-Gd(1)-O(4)	69.2(4)	N(1)-Cu(1)-O(2)	175.3(5)
O(1)-Gd(1)-N(4)	135.3(4)	O(1)-Gd(1)-O(3)	61.9(3)	N(1)-Cu(1)-O(1)	95.3(5)
O(9)-Gd(1)-N(4)	72.4(4)	O(9)-Gd(1)-O(3)	80.3(3)	O(2)-Cu(1)-O(1)	83.4(4)
O(2)-Gd(1)-N(4)	134.8(4)	O(2)-Gd(1)-O(3)	125.6(4)	N(1)-Cu(1)-N(2)	85.7(6)
O(8)-Gd(1)-N(4)	140.3(4)	O(8)-Gd(1)-O(3)	105.8(4)	O(2)-Cu(1)-N(2)	94.5(5)
O(5)-Gd(1)-N(4)	74.1(4)	O(5)-Gd(1)-O(3)	66.5(4)	O(1)-Cu(1)-N(2)	167.0(5)
O(1)-Gd(1)-O(6)	145.3(3)	N(4)-Gd(1)-O(3)	80.0(4)	N(1)-Cu(1)-Cl(1)	87.1(4)
O(9)-Gd(1)-O(6)	136.1(4)	O(6)-Gd(1)-O(3)	115.6(4)	O(2)-Cu(1)-Cl(1)	97.5(3)
O(2)-Gd(1)-O(6)	115.4(4)	O(4)-Gd(1)-O(3)	157.3(3)	O(1)-Cu(1)-Cl(1)	94.6(3)

Table S3 The Ln^{III} center of geometry analysis for complexes **1-2** by SHAPE software

Atom	EP-9	OPY-9	HBPY-9	JTC-9	JCCU-9	CCU-9	JCSAPR-9
Ho1	33.293	23.204	15.634	14.843	9.023	7.373	3.826
Gd1	32.833	23.092	15.808	14.780	8.987	7.434	3.986
Atom	CSAPR-9	JTCTPR-9	TCTPR-9	JTDIC-9	HH-9	MFF-9	
Ho1	3.079	4.623	4.077	12.275	5.880	2.243	
Gd1	3.220	4.615	4.211	12.371	5.863	2.298	

EP-9	1	D_{9h}	Enneagon
OPY-9	2	C_{8v}	Octagonal pyramid
HBPY-9	3	D_{7h}	Heptagonal bipyramid
JTC-9	4	C_{3v}	Johnson triangular cupola J3
JCCU-9	5	C_{4v}	Capped cube J8
CCU-9	6	C_{4v}	Spherical-relaxed capped cube
JCSAPR-9	7	C_{4v}	Capped square antiprism J10
CSAPR-9	8	C_{4v}	Spherical capped square antiprism
JTCTPR-9	9	D_{3h}	Tricapped trigonal prism J51
TCTPR-9	10	D_{3h}	Spherical tricapped trigonal prism
JTDIC-9	11	C_{3v}	Tridiminished icosahedron J63
HH-9	12	C_{2v}	Hula-hoop
MFF-9	13	C_s	Muffin

Table S4 The Cu^{II} center of geometry analysis for complexes **1-2** by SHAPE software.

Complex	PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5
1	31.404	3.526	5.289	1.687	9.582
2	30.917	3.356	5.460	1.640	9.847

PP-5	1	D_{5h}	Pentagon
vOC-5	2	C_{4v}	Vacant octahedron
TBPY-5	3	D_{3h}	Trigonal bipyramid
SPY-5	4	C_{4v}	Square pyramid
JTBPY-5	5	D_{3h}	Johnson trigonal bipyramid J12

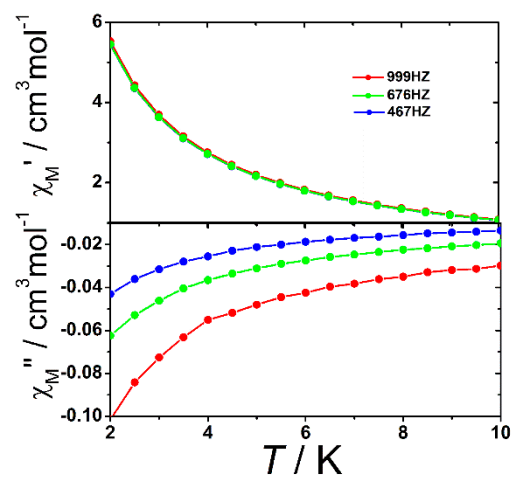


Figure S1 Temperature dependent ac susceptibilities of complex **2** at different frequencies under $H_{ac} = 2$ Oe and $H_{dc} = 0$ Oe

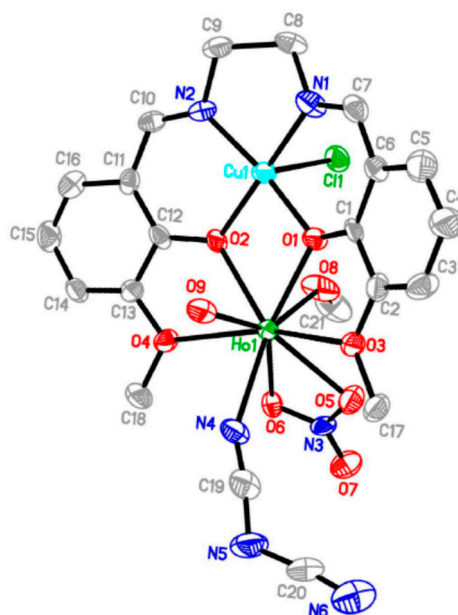


Figure S2 A view of the molecular structure of complex **1**. Thermal ellipsoids are depicted at 30% probability.

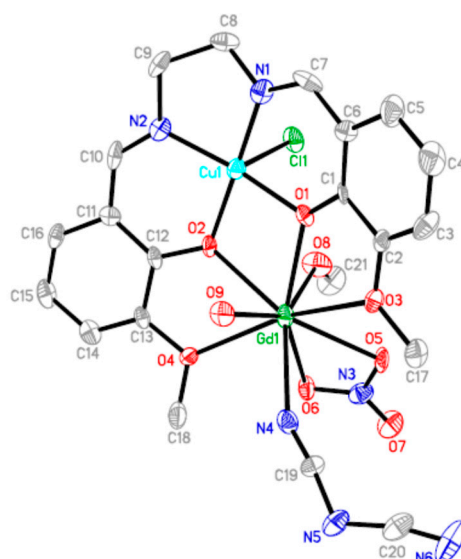


Figure S3 A view of the molecular structure of complex **2**. Thermal ellipsoids are depicted at 30% probability

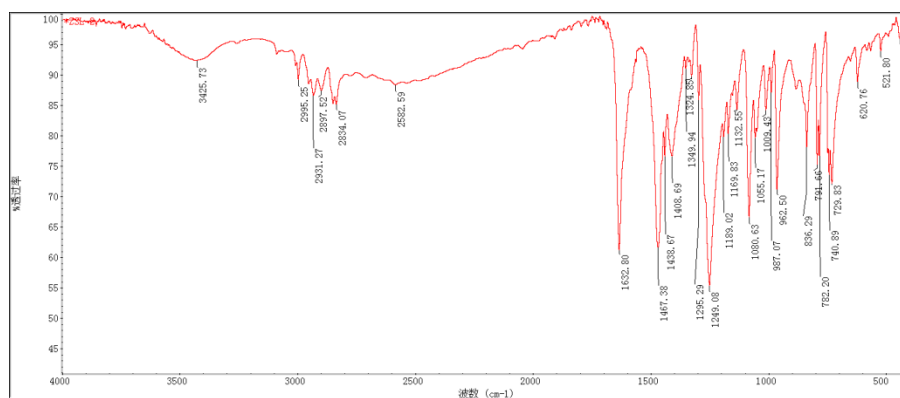


Fig. S4 The IR spectra of the H₂L Ligand

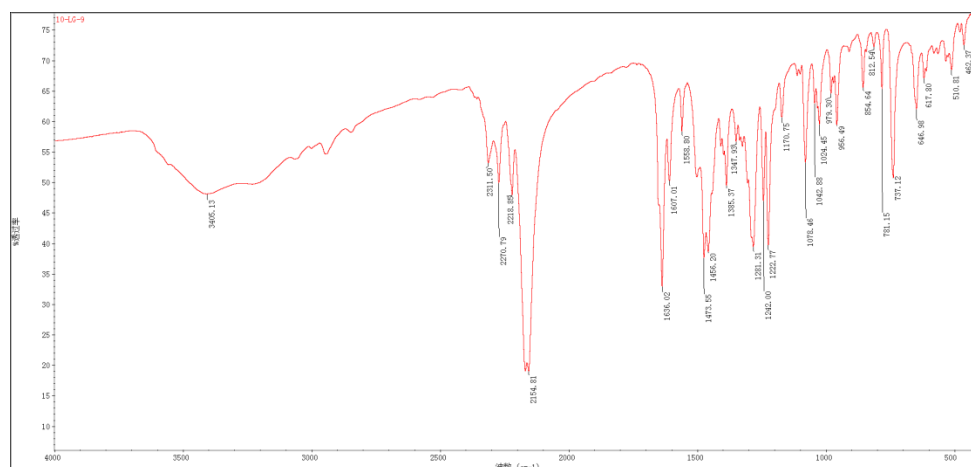


Fig. S5 The IR spectra of complex **1**.

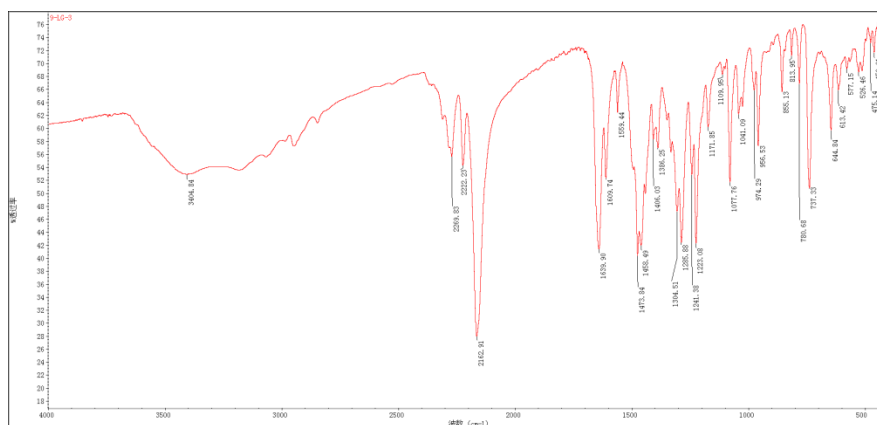


Figure S6 The IR spectra of complex 2.

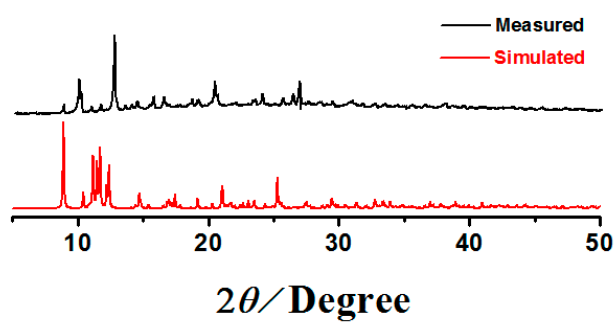


Figure S7 The powder XRD of complex 1.

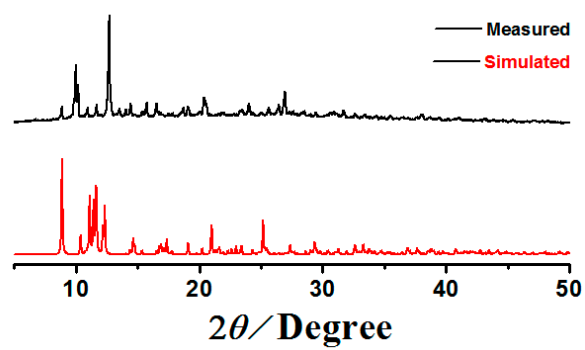


Figure S8 The powder XRD of complex 2.