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Synthesis, structures and magnetism of heterotrimetallic Ni-Cu-Ln complexes based on a dicompartmental imine-oxime ligand

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Tble S1 Selected bond lengths (Å) and angles (°) for **1**

Cu1-N4	1.927(9)	Ni1-O4A	2.208(7)
Cu1-O2	1.931(7)	Gd1-O8	2.352(7)
Cu1-O3	1.961(4)	Gd1-O7	2.364(7)
Cu1-N1	1.963(9)	Gd1-O11	2.367(7)
Cu1-O14	2.624(4)	Gd1-O9	2.385(8)
Ni1-N2	1.991(9)	Gd1-O12	2.389(7)
Ni1-O3	1.994(6)	Gd1-O6	2.481(7)
Ni1-N3	2.004(9)	Gd1-O5	2.344(7)
Ni1-O2	2.049(7)	Gd1-O10	2.412(7)
Ni1-O13	2.241(8)		
N4-Cu1-O2	165.7(3)	O5-Gd1-O12	120.2(2)
N4-Cu1-O3	87.2(3)	O5-Gd1-O10	147.1 (2)
N4-Cu1-N1	101.5(4)	O5-Gd1-O6	69.1(2)
O2-Cu1-O3	84.0(3)	O8-Gd1-O7	71.1(2)
O2-Cu1-N1	86.9(3)	O8-Gd1-O11	145.8(2)
O3-Cu1-N1	170.9(3)	O8-Gd1-O9	122.4(3)
N2-Ni1-O3	168.4(3)	O8-Gd1-O12	79.4(2)
N2-Ni1-N3	101.3(4)	O8-Gd1-O10	78.3(2)
N2-Ni1-O2	88.2(3)	O8-Gd1-O6	72.7(2)
N2-Ni1-O4A	93.1(3)	O7-Gd1-O11	142.7(2)
N2-Ni1-O13	83.7(3)	O7-Gd1-O9	73.3(3)
O3-Ni1-N3	90.2(3)	O7-Gd1-O12	149.3(2)

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O3-Ni1-O2	80.2(3)	O7-Gd1-O10	105.4(3)
O3-Ni1-O4A	88.1(3)	O7-Gd1-O6	85.9(2)
O3-Ni1-O13	89.4(3)	O11-Gd1-O9	77.5(3)
N3-Ni1-O2	169.0(3)	O11-Gd1-O12	67. 7(2)
N3-Ni1-O4A	91.9(3)	O11-Gd1-O10	85.0(3)
N3-Ni1-O13	90.8(3)	O11-Gd1-O6	107.1(3)
O2-Ni1-O4A	93.1(3)	O9-Gd1-O12	132.6(2)
O2-Ni1-O13	83.7(3)	O9-Gd1-O10	69.4 (2)
O4A-Ni1-O13	176.2(3)	O9-Gd1-O6	146.1(2)
O5-Gd1-O7	75.4(2)	O12-Gd1-O10	76.26(0)
O5-Gd1-O11	77.1(2)	O12-Gd1-O6	77.0 (2)
O5-Gd1-O9	79.7(2)	O10-Gd1-O6	143.4(2)

Symmetry transformations used to generate equivalent atoms: A: -x+1,-y,-z+1.

Table S2 Selected bond lengths (Å) and angles (°) for **2**

Cu1-O3	1.946(3)	Ni1-O13	2.160(5)
Cu1-N4	1.949(4)	Tb1-O8	2.389(4)
Cu1-N1	1.950(5)	Tb1-O5	2.350(4)
Cu1-O2	1.963(3)	Tb1-O9	2.359(3)
Cu1-O14	2.460(4)	Tb1-O7	2.335(4)
Ni1-N2	2.003(5)	Tb1-O11	2.371(4)
Ni1-O3	2.014(3)	Tb1-O10	2.346(4)
Ni1-O2	2.044(4)	Tb1-O12	2.358(4)
Ni1-N3	2.011(5)	Tb1-O6	2.411(4)
Ni1-O4A	2.109(4)	O5- Tb1-O12	146.67(1)
N4-Cu1-O2	166.14(2)	O5- Tb1-O6	71.31(1)
N4-Cu1-N1	98.22(2)	O7- Tb1-O8	71.17(3)
O3-Cu1-O14	95.61(7)	O7- Tb1-O5	76.25(1)
O3-Cu1-O2	80.47(2)	O7- Tb1-O11	74.62(1)
O3-Cu1-N4	90.15(2)	O7- Tb1-O9	142.29(1)
O3-Cu1-N1	170.81(2)	O7- Tb1-O12	110.79(1)
N1-Cu1-O2	90.62(2)	O7- Tb1-O10	145.33(1)
N2-Ni1-O3	168.1 (2)	O7- Tb1-O6	85.16(1)
N2-Ni1-N3	99.4(2)	O8- Tb1-O6	75.36(1)
N2-Ni1-O2	91.19(2)	O9- Tb1-O8	146.13(1)
N2-Ni1-O4A	94.19(2)	O9- Tb1-O6	106.40(1)
O3-Ni1-O2	76.92(2)	O11-Tb1-O8	119.40(1)
O3-Ni1-O4A	89.13(2)	O11-Tb1-O6	147.77(1)
O3-Ni1-O13	85.66(2)	O10-Tb1-O12	74.35(1)
N3-Ni1-O3	92.44(2)	O10-Tb1-O9	71.19(1)
N3-Ni1-O2	168.41(2)	O10-Tb1-O11	135.81(1)
N3-Ni1-O4A	90.18(2)	O10-Tb1-O8	77.47(1)
N3-Ni1-O13	86.5(2)	O10-Tb1-O6	72.79(1)
O2-Ni1-O4A	94.19(1)	O10-Tb1-O12	74.35(1)

O2-Ni1-O13	88.1(2)	O10-Tb1-O5	119.12(1)
O4A-Ni1-O13	173.66(2)	O12-Tb1-O11	71.70(1)
O5-Tb1-O8	134.70(1)	O12-Tb1-O8	75.90(1)
O5-Tb1-O11	79.54(1)	O12-Tb1-O6	140.06(1)
O5- Tb1-O9	74.04(1)	O12-Tb1-O9	83.49(1)

Symmetry transformations used to generate equivalent atoms: A: -x+2,-y+2,-z+1.

Table S3 Selected bond lengths (Å) and angles (°) for **3**

Cu1-N1	1.933(7)	Ni1-O13	2.149(7)
Cu1-O3	1.941(5)	Dy1-O5	2.329(5)
Cu1-N4	1.953(6)	Dy1-O8	2.361(5)
Cu1-O2	1.954(5)	Dy1-O7	2.330(5)
Cu1-O14	2.444(8)	Dy1-O11	2.346(5)
Ni1-N2	1.999(7)	Dy1-O9	2.353(6)
Ni1-O3	2.014(5)	Dy1-O12	2.334(5)
Ni1-N3	2.003(8)	Dy1-O6	2.408(6)
Ni1-O2	2.037(5)	Dy1-O10	2.360 (5)
Ni1-O4A	2.118(5)	O5-Dy1-O8	135.09(5)
N1-Cu1-O2	90.5(2)	O5-Dy1-O10	146.43(2)
N1-Cu1-O3	170.9(3)	O5-Dy1-O6	71.34(2)
O3-Cu1-O2	80.6(2)	O7-Dy1-O6	85.2(2)
O3-Cu1-N4	90.2(2)	O7-Dy1-O11	142.31(2)
N4-Cu1-O2	167.0(2)	O7-Dy1-O9	74.76(2)
N2-Ni1-O3	168.75(0)	O7-Dy1-O12	145.38(2)
N2-Ni1-N3	98.7(3)	O7-Dy1-O8	71.32(2)
N2-Ni1-O2	91.8(3)	O7-Dy1-O10	108.7(2)
N2-Ni1-O13	95.4(3)	O8-Dy1-O6	75.53(2)
N2-Ni1-O4A	93.9(2)	O9-Dy1-O6	147.09(2)
O3-Ni1-O2	76.9(2)	O9-Dy1-O8	120.2(2)
O3-Ni1-O4A	89.2(2)	O9-Dy1-O10	71.28(2)
O3-Ni1-O13	84.0(2)	O10-Dy1-O8	75.04(2)
N3-Ni1-O3	92.5(3)	O10-Dy1-O6	141.01(2)
N3-Ni1-O2	168.0(3)	O11-Dy1-O10	85.52(2)
N3-Ni1-O4A	91.6(3)	O11-Dy1-O9	77.5(2)
N3-Ni1-O13	84.5(3)	O11-Dy1-O8	146.04(2)
O4A-Ni1-O13	172.0(2)	O11-Dy1-O6	105.81(2)
O2-Ni1-O13	88.7(3)	O12-Dy1-O11	71.22(2)
O5- Dy1-O7	76.42(1)	O12-Dy1-O8	76.96(2)
O5- Dy1-O12	120.0(2)	O12-Dy1-O6	73.68(2)
O5- Dy1-O11	73.50(2)	O12-Dy1-O9	135.35(2)
O5- Dy1-O9	78.66(2)	O12- Dy1-O10	75.21(2)

Symmetry transformations used to generate equivalent atoms: A: -x+2,-y+2,-z+1.

Table S4 Selected bond lengths (Å) and angles (°) for **4**

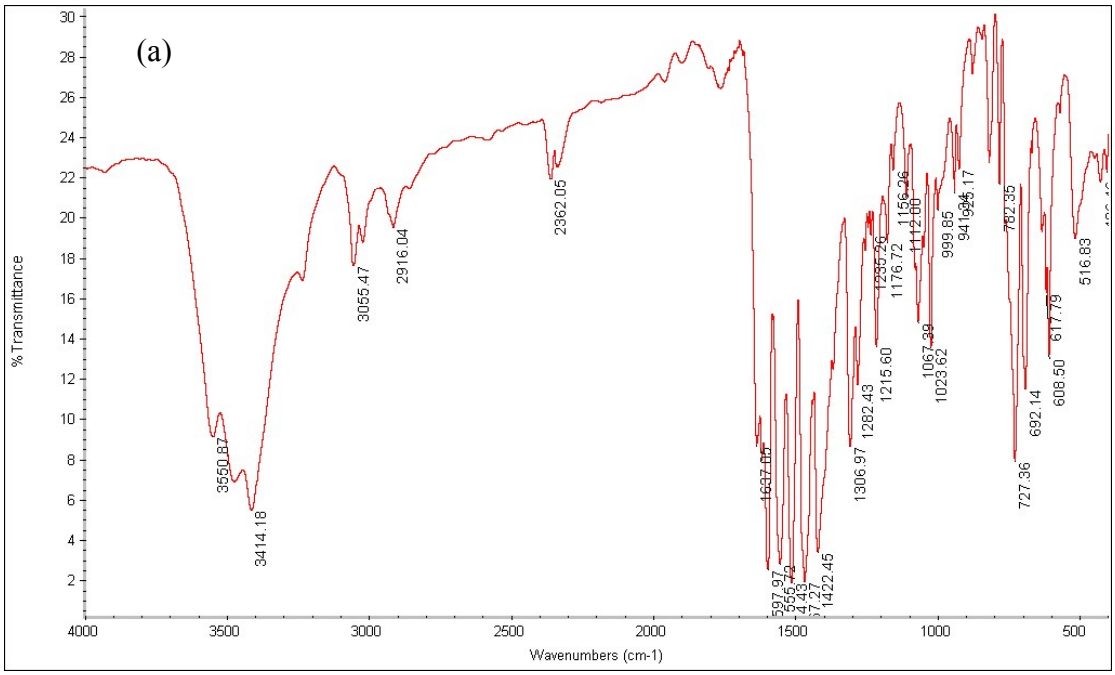
Cu1-N1	1.942(5)	Ni1-O13	2.146(4)
Cu1-O3	1.950(4)	Ho1-O7	2.299(1)
Cu1-N4	1.947(5)	Ni1-O13	2.146(6)
Cu1-O2	1.964(4)	Ho1-O5	2.331 (4)
Cu1-O14	2.418(4)	Ho1-O8	2.368(4)
Ni1-N2	1.996(6)	Ho1-O9	2.346(4)
Ni1-O3	2.022(4)	Ho1-O10	2.319(5)
Ni1-N3	2.015(6)	Ho1-O11	2.344(5)
Ni1-O2	2.041(4)	Ho1-O12	2.336(4)
Ni1-O4A	2.104(4)	Ho1-O6	2.388(5)
N1-Cu1-O2	91.1(2)	O5-Ho1-O8	135.54(2)
N1-Cu1-O3	171.2(2)	O5-Ho1-O11	78.45(2)
N1-Cu1-N4	97.9(2)	O7-Ho1-O5	76.22(2)
O3-Cu1-O2	80.37(2)	O7-Ho1-O6	85.03(2)
N4-Cu1-O3	90.14(2)	O7-Ho1-O11	74.42(2)
N4-Cu1-O2	166.28(2)	O7-Ho1-O9	141.60(2)
N2-Ni1-O3	168.4(2)	O7-Ho1-O12	110.64(2)
N2-Ni1-N3	98.9(2)	O7-Ho1-O8	72.03(2)
N2-Ni1-O2	91.5(2)	O7-Ho1-O10	145.42(2)
N2-Ni1-O13	93.0(5)	O8-Ho1-O6	75.06(2)
N2-Ni1-O4A	92.5(2)	O9-Ho1-O6	106.73(2)
O3-Ni1-O2	76.87(2)	O9-Ho1-O8	145.95(2)
O3-Ni1-O4A	89.11(2)	O10- Ho1-O12	74.34(2)
O3-Ni1-O13	86.2(2)	O10- Ho1-O8	76.69(2)
N3-Ni1-O3	92.6(2)	O10-Ho1-O11	136.14(2)
N3-Ni1-O2	168.3(2)	O10-Ho1-O5	119.35(2)
N3-Ni1-O4A	90.7(2)	O10-Ho1-O6	72.87(2)
N3-Ni1-O13	85.1(3)	O10-Ho1-O9	71.75(2)
O2-Ni1-O4A	94.03(2)	O11-Ho1-O9	77.03(2)
O2-Ni1-O13	89.2(3)	O11-Ho1-O8	120.34(2)
O4A-Ni1-O13	173.5(2)	O11-Ho1-O6	147.21(2)
O5-Ho1-O6	71.91(2)	O12-Ho1-O11	72.42(4)
O5-Ho1-O12	149.48(2)	O12-Ho1-O6	139.80(2)
O5-Ho1-O9	73.32(2)	O12-Ho1-O9	84.08(3)

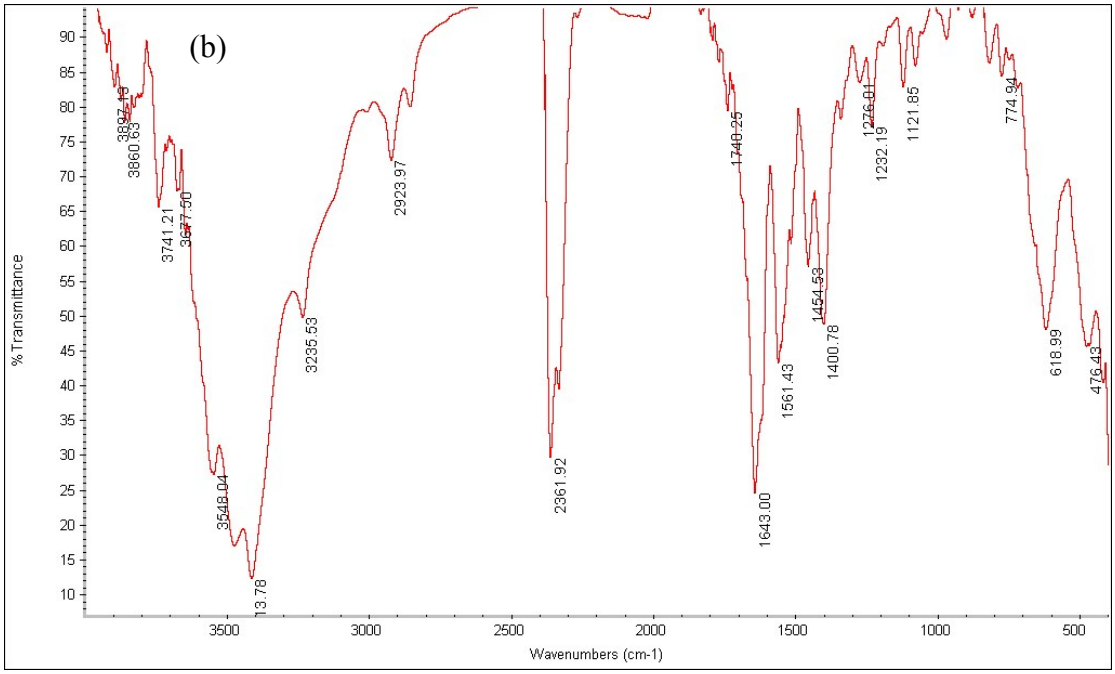
Symmetry transformations used to generate equivalent atoms: A: -x+1,-y+2,-z+1.

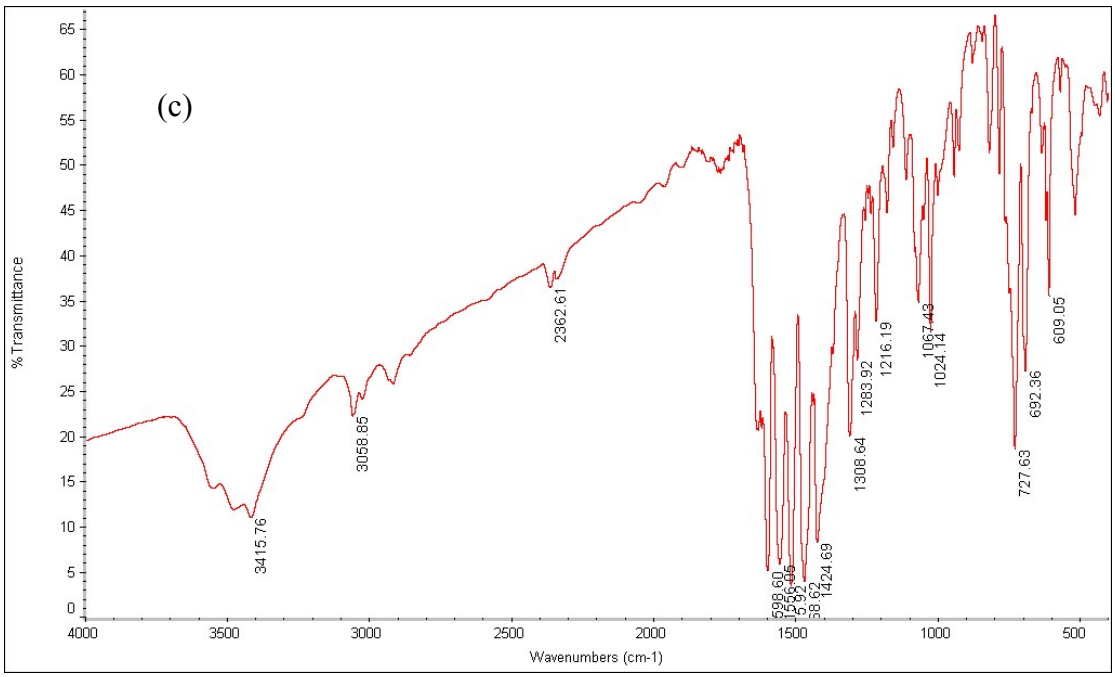
Table S5. Results of the Continuous Shape Measure Analysisa geometry[a]

Geometry	CU-8	SAPR-8	TDD-8
1	8.15	1.04	**0.87**
2	8.34	**0.59**	1.12
3	8.45	**0.68**	0.95
4	8.44	**0.56**	1.08

[a]CU-8 is the shape measure relative to the cube; SAPR-8 is the shape measure relative to the square antiprism; TDD-8 is the shape measure relative to the triangular dodecahedron. The number in bold corresponds to the closer ideal geometry to the real complexes.




(b)
% Transmittance
Wavenumbers (cm-1)
3860.63
3741.21
3548.04
3235.53
2923.97
2361.92
1643.00
1561.43
1454.53
1400.78
1276.01
1232.19
1121.85
774.94
618.99
476.43


(c)
% Transmittance
Wavenumbers (cm-1)
3415.76
3058.85
2362.61
1598.60
1424.69
1308.64
1283.92
1216.19
1067.43
1024.14
727.63
692.36
609.05

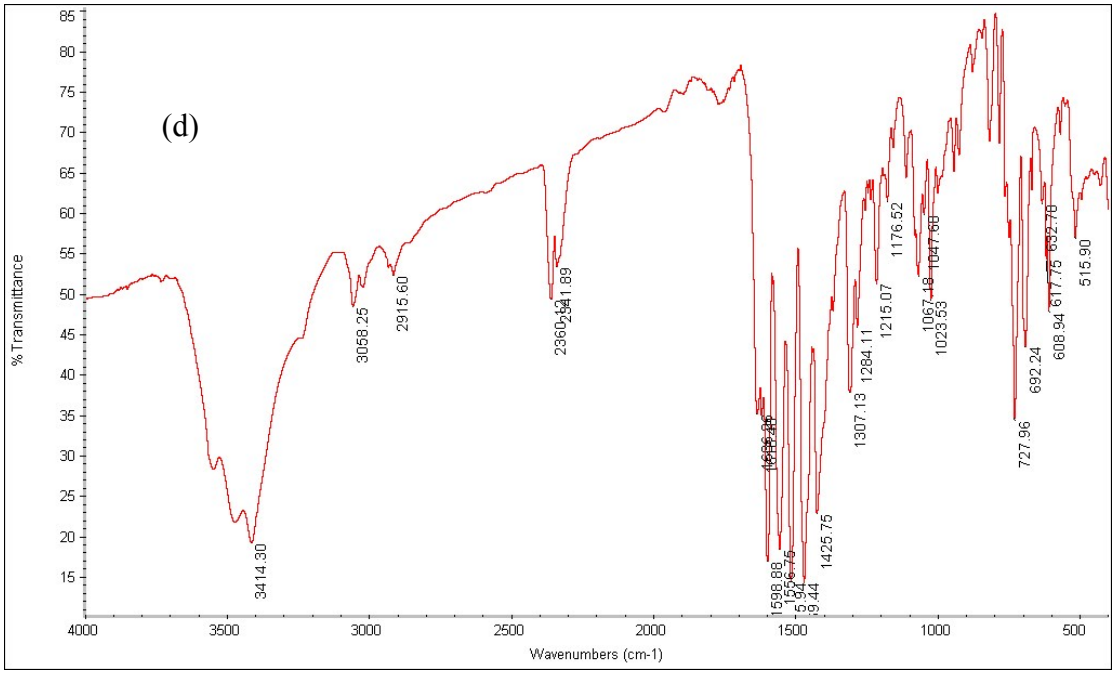
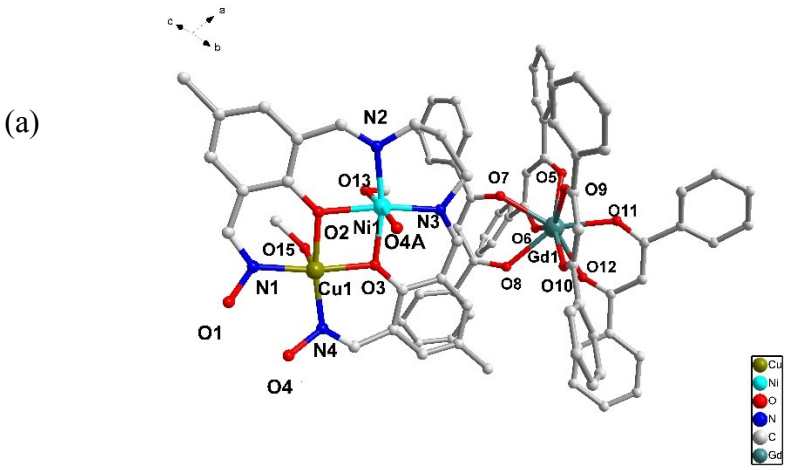
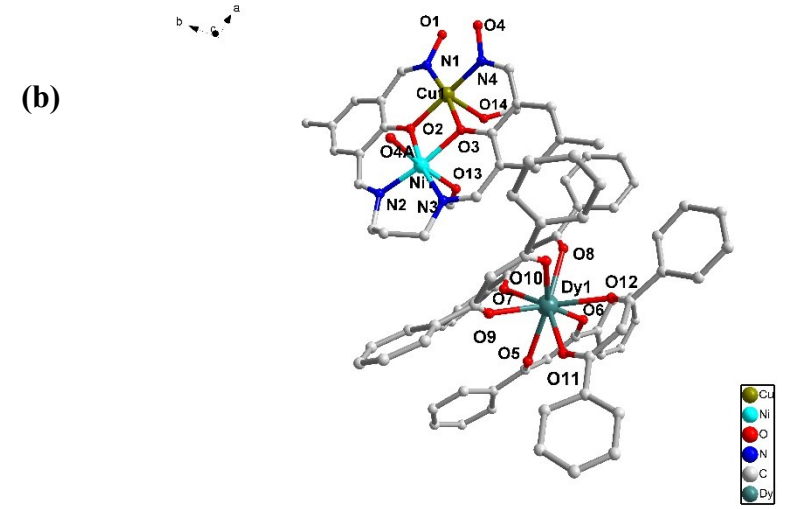


Figure S1. (a)-(d): The IR spectra of compounds **1-4**, respectively.





(c)

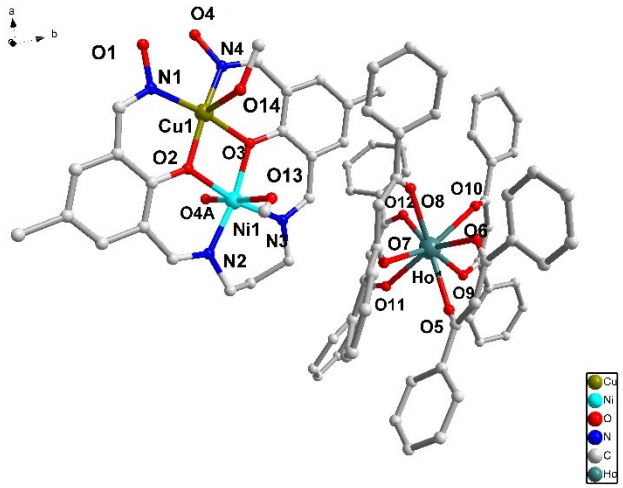


Figure S2. Perspective drawing of the crystallographically structural unit of **1** (a), **3** (b) and **4** (c) showing the atom numbering. H atoms and solvent molecules are omitted for clarity

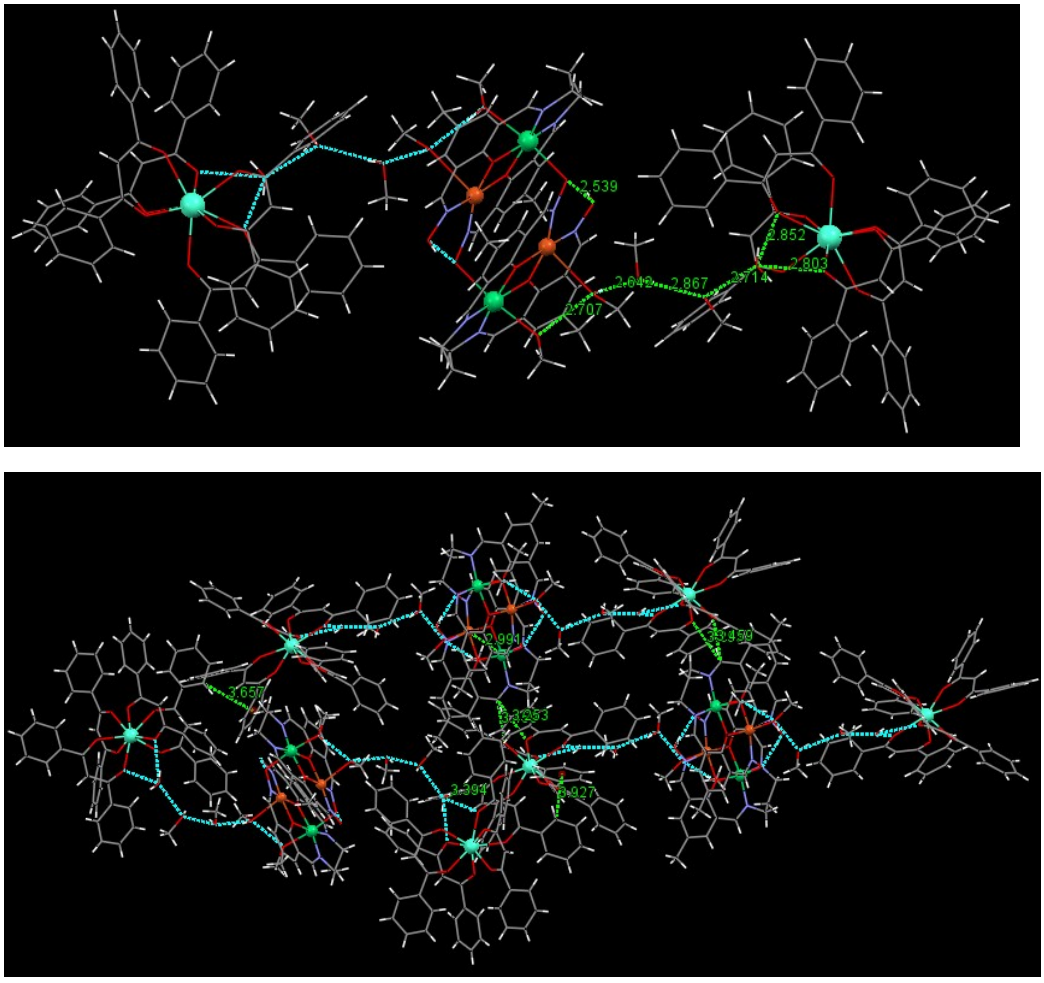


Figure S3. Up: The dimeric $[Ni(MeOH)(HL)Cu(MeOH)]_2^{2+}$ cation in **1** is linked to two $[Gd(dbm)_4]^-$ anions by two H_2O molecules and four methanol molecules with O–H···O H-bonding interactions. Down: A view showing 3D structure formed by weak O–H···O, C–H···C and C–H···π interactions in **1**.

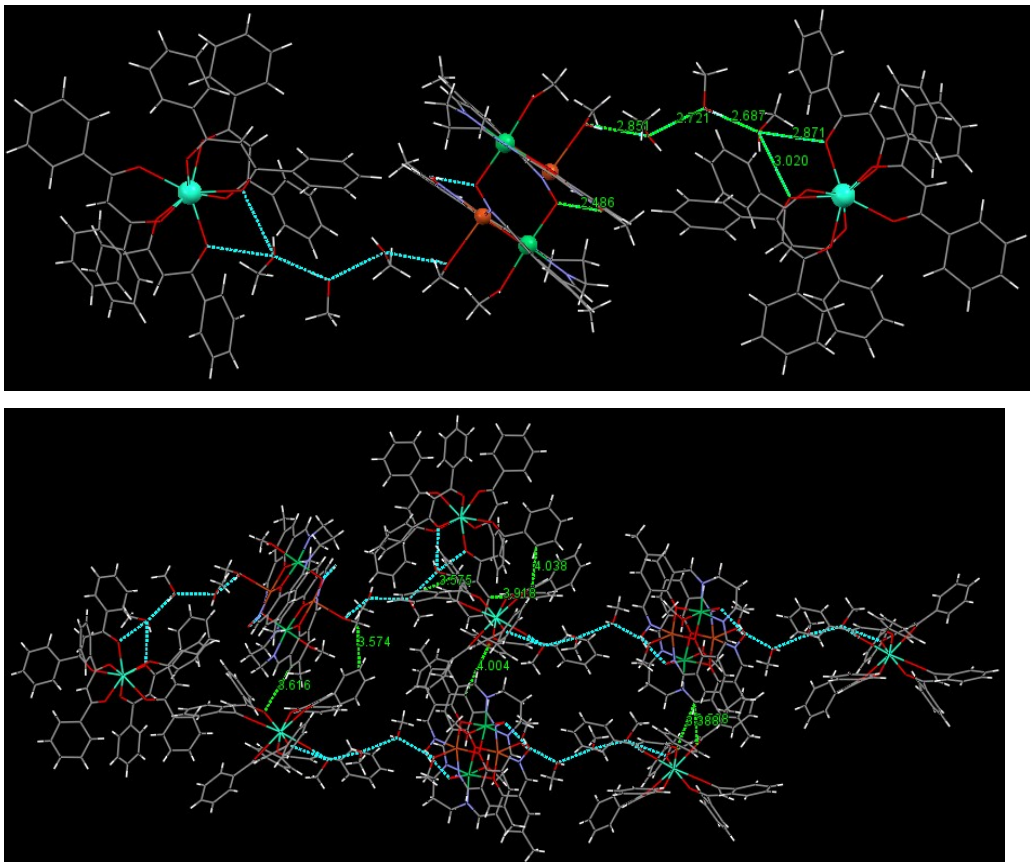


Figure S4. Up: The dimeric $[Ni(MeOH)(HL)Cu(MeOH)]_2^{2+}$ cation in **2-4** is linked to two $[Ln(dbm)_4]^-$ anions by six methanol molecules with O–H···O H-bonding interactions. Down: A view showing 3D structure formed by weak O–H···O, C–H···C and C–H···π interactions in **2-4**.

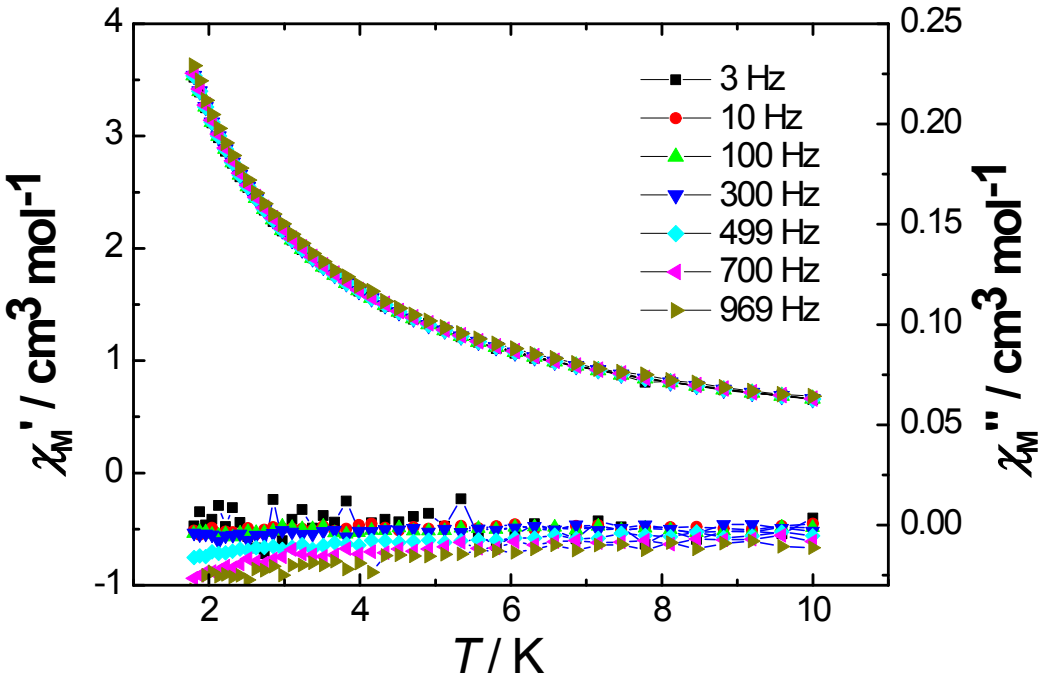


Figure S5. Temperature dependence of the in-phase χ' and out-of-phase χ'' at different frequencies in a 3 Oe ac field oscillating at 3–969 Hz with a zerodc field for **2**.

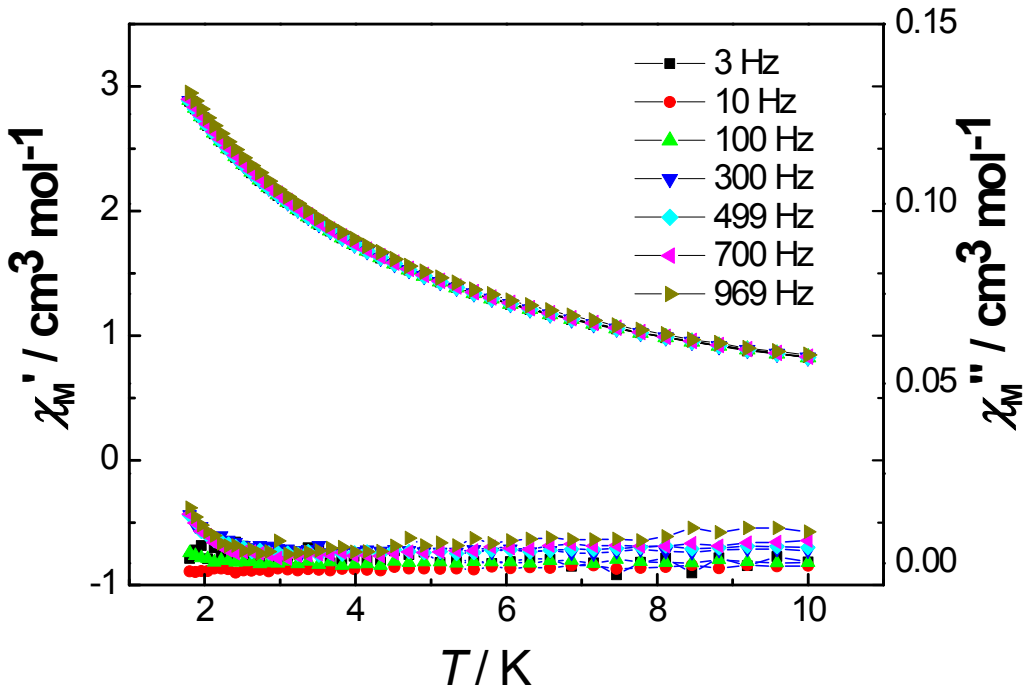


Figure S6. Temperature dependence of the in-phase χ' and out-of-phase χ'' at different frequencies in a 3 Oe ac field oscillating at 3–969 Hz with a zerodc field for **4**.