Supporting Information

Structural Variations in $(CuL)_2Ln$ Complexes of a Series of Lanthanide Ions withSalen-Type Unsymmetrical Schiff Base(H_2L): The Dy and Tb Derivatives as Potential Single-Molecule Magnets

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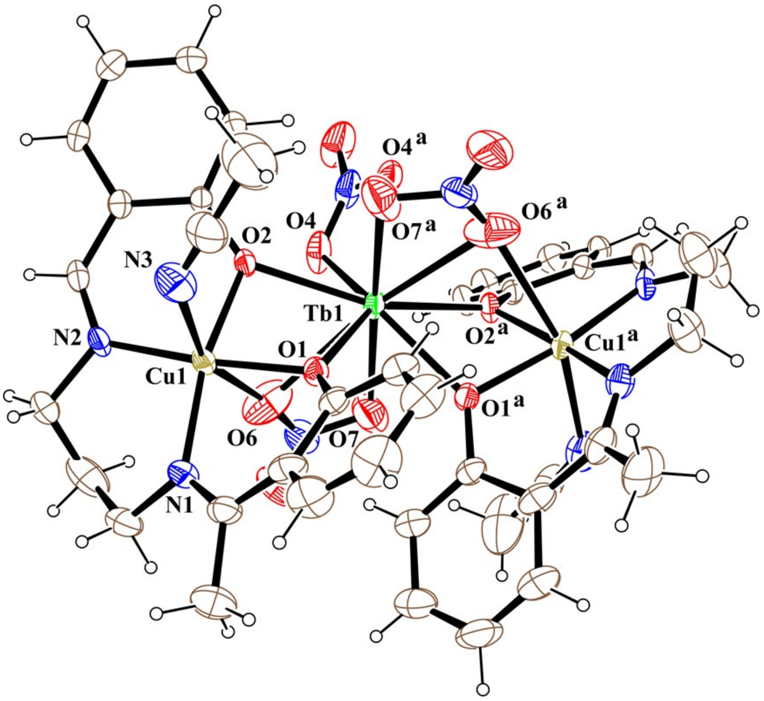


Fig. S1. The structures of **2** with thermal ellipsoids at 20% probability.

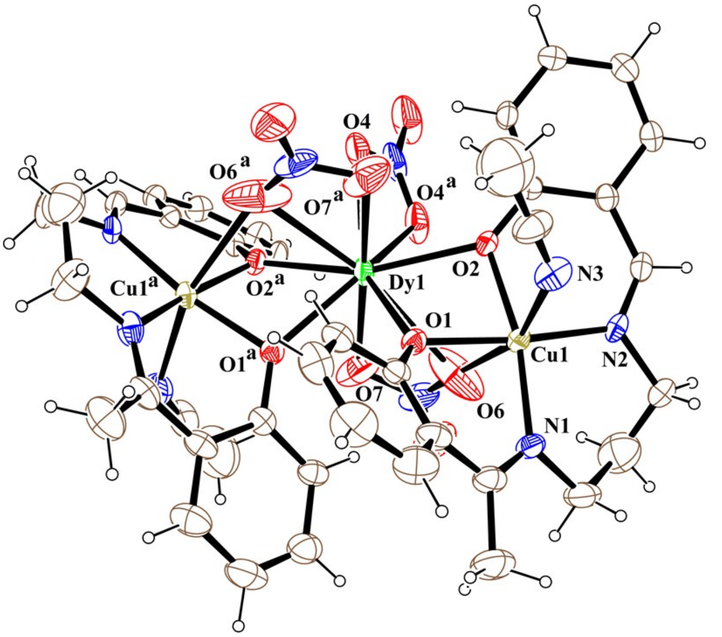


Fig. S2. The structures of **3** with thermal ellipsoids at 20% probability.

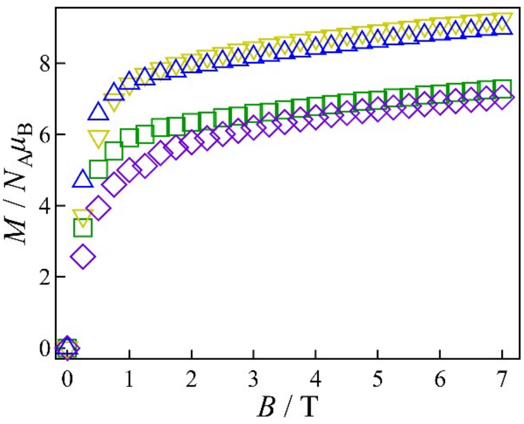


Fig. S3. Magnetization curves for **2** (green squares), **3** (blue triangles), **4** (purple diamonds), and **5** (yellow inverted triangles), measured at 1.8 K.

(a) (b)

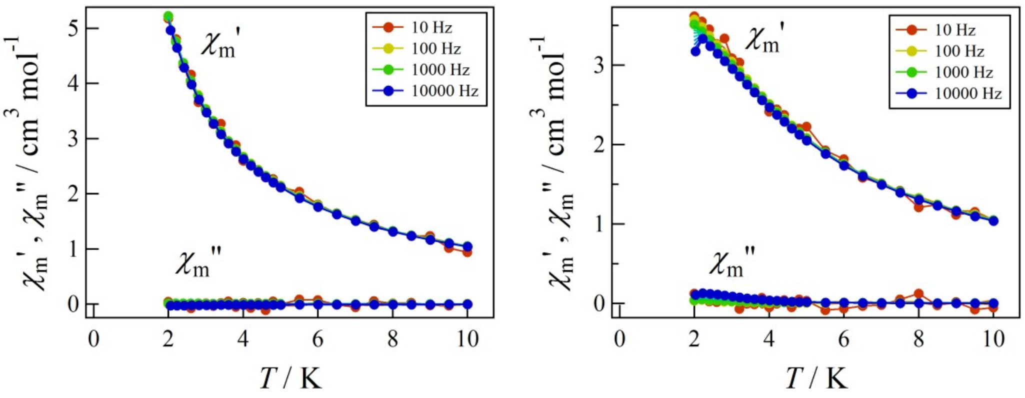
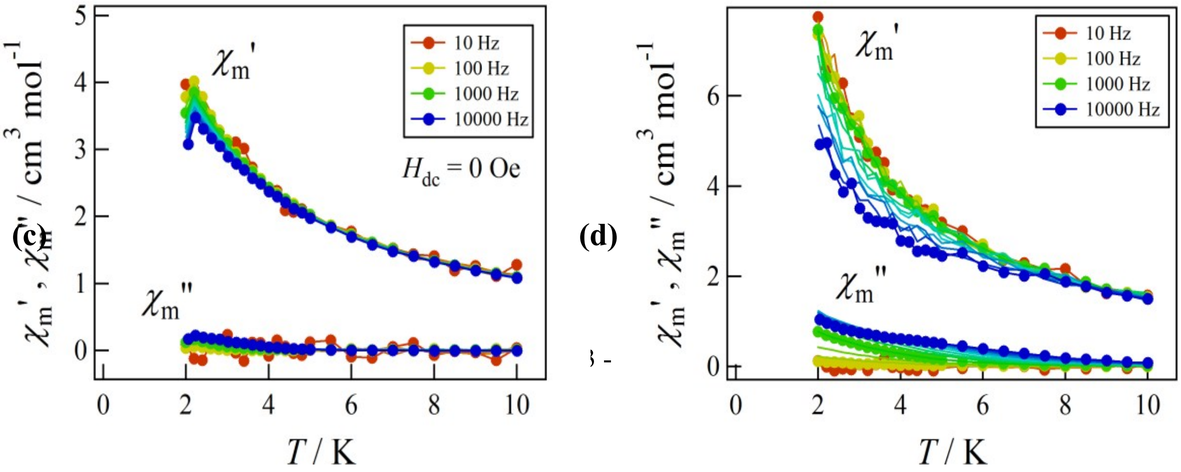


Fig. S4. The ac magnetic susceptibilities measured for **1** at applied dc bias fields of (a) 0 Oe and (b) 2000 Oe.

(a) (b)



(c) (d)

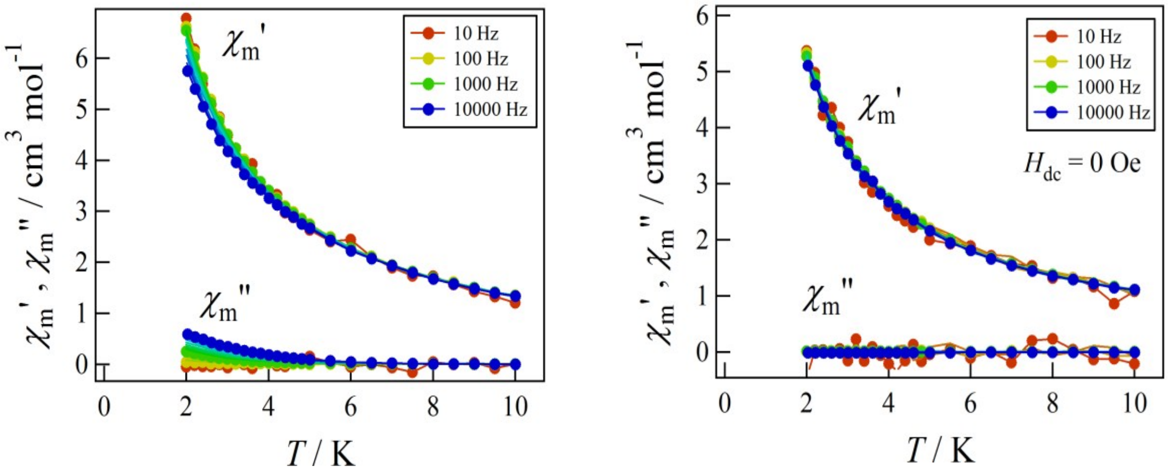


Fig. S5. The ac magnetic susceptibilities measured for (a) **2**, (b) **3**, (c) **4**, and (d) **5** in zero dc field.

Table S1. Bond distances (Å) and angles (°) for complex **1–3.**

	1(M= Gd)	2(M=Tb)	3(M=Dy)
Cu1 - O1	1.956(6)	1.956(4)	1.963(5)
Cu1 - N2	1.973(8)	1.967(5)	1.978(7)
Cu1 - O2	1.975(6)	1.970(4)	1.982(6)
Cu1 - N1	2.013(8)	2.000(5)	2.002(8)
Cu1 - N3	2.354(14)	2.442(10)	2.441(12)
Cu1 - O6	2.601(12)	2.561(10)	2.560(12)
M1 - O1	2.369(5)	2.353(4)	2.337(5)
M1 - O2	2.408(5)	2.392(4)	2.376(5)
M1 - O4	2.521(7)	2.501(5)	2.520(8)
M1 - O7	2.666(11)	2.650(8)	2.653(12)
M1 – O6	2.730(9)	2.685(9)	2.756(13)

O1 - Cu1 - N2	171.3(3)	172.0(2)	171.6(2)
O1 - Cu1 - O2	81.7(2)	80.9(2)	81.0(2)
N2 - Cu1 - O2	90.9(3)	91.8(2)	91.5(3)
O1 - Cu1 - N1	89.2(3)	89.7(2)	89.8(3)
N2 - Cu1 - N1	97.3(3)	97.0(2)	97.1(3)
O2 - Cu1 - N1	167.7(3)	167.5(2)	168.2(3)
O1 - Cu1 - N3	89.3(3)	89.0(2)	89.0(3)
N2 - Cu1 - N3	95.0(4)	93.9(3)	94.6(4)
O2 - Cu1 - N3	86.9(3)	86.5(2)	87.6(3)
N1 - Cu1 - N3	101.3(4)	101.7(3)	99.6(4)
O1 – Cu1 – O6	78.4(4)	78.7(4)	79.6(4)
O2 – Cu1 – O6	76.9(4)	76.3(4)	77.3(4)
N1 – Cu1 – O6	93.1(4)	93.8(4)	93.9(4)
N2 – Cu1 – O6	95.5(4)	96.4(4)	95.0(4)
N3 – Cu1 – O6	160.8(4)	160.2(4)	162.3(4)
O1 - M1 - O1^{a}	73.1(3)	73.2(2)	72.6(3)
O1 - M1 - O2^{a}	138.2(2)	138.13(13)	138.5(2)
O1 - M1 - O2	65.2(2)	64.91(14)	65.9(2)
O2 - M1 - O2^{a}	156.6(3)	157.0(2)	155.7(3)
O1 - M1 - O4^{a}	142.8(2)	142.4(2)	142.5(2)
O1 - M1 - O4	131.9(2)	131.64(15)	132.2(2)
O2 - M1 - O4^{a}	85.4(2)	85.67(14)	85.0(2)
O2 - M1 - O4	73.3(2)	73.38(15)	72.8(2)
O4 - M1 - O4^{a}	48.8(5)	49.8(3)	49.3(4)
O1 - M1 - O7^{a}	75.3(3)	75.5(2)	76.0(3)
O2 - M1 - O7^{a}	70.4(3)	70.4(2)	71.8(3)
O4 - M1 - O7^{a}	112.8(3)	112.7(2)	113.1(3)
O1 - M1 - O7^{a}	75.3(3)	75.5(2)	76.0(3)
O1 - M1 - O7	99.3(3)	99.9(2)	99.1(3)
O2 - M1 - O7^{a}	70.4(3)	70.4(2)	71.8(3)
O2 - M1 - O7	111.0(3)	110.9(2)	109.5(2)
O4 - M1 - O7	73.5(3)	72.7(2)	72.7(3)
O7 - M1 - O7^{a}	173.5(5)	174.4(3)	174.1(5)
O1 - M1 - O6^{a}	98.3(3)	98.64(14)	98.0(3)
O2 - M1 - O6^{a}	115.2(3)	115.3(2)	115.8(3)
O4 - M1 - O6^{a}	121.4(3)	121.4(2)	121.6(3)

O7 - M1 - O6[a]	133.7(4)	133.8(2)	134.7(4)
O1 - M1 - O6	69.5(3)	70.0(2)	69.7(3)
O2 -M1 - O6	68.1(3)	67.7(2)	67.6(3)
O4 - M1 - O6	73.3(3)	72.3(2)	73.1(3)
O7 - M1 - O6	45.1(4)	45.2(2)	44.2(4)
O6 - M1 - O6[a]	165.3(5)	166.3(3)	165.2(5)
Cu1 - O1 - M1	100.5(2)	100.4(2)	100.3(2)
Cu1 - O2 – M1	98.6(2)	98.7(2)	98.4(2)
Cu1 - O6 – M1	77.4(2)	78.5(2)	77.0(4)

Symmetry element 1-x, ½-y,z

Table S2 Dimensions (distances, Å, angles, deg) in the coordination sphere of **4.**

Cu1 - N2	1.919(6)
Cu1 - O1	1.929(5)
Cu1 - O2	1.986(5)
Cu1 - N1	1.997(6)
Ho1 - O3A	2.506(12)
Ho1 - O2	2.180(6)
Ho1 - O1	2.182(6)
Ho1 - O5[a]	2.340(6)
Ho1 - O1[a]	2.430(5)
Ho1 - O3B[a]	2.474(13)
Ho1 - O6[a]	2.518(14)
Ho1 - O2[a]	2.566(8)
Ho1 - O5	2.604(6)
N2 - Cu1 - O1	172.8(3)
N2 - Cu1 - O2	92.1(3)
O1 - Cu1 - O2	84.7(2)
N2 - Cu1 - N1	95.9(3)

O1- Cu1 - N1	89.2(2)
O2 - Cu1 - N1	159.8(2)
O3B^a – Ho1 – O1	105.3(4)
O3B^a – Ho1 – O2	130.2(3)
O3B^a – Ho1 – O5	72.0(3)
O3B^a – Ho1 – O1^a	119.4(4)
O3B^a – Ho1 – O2	130.2(3)
O3B^a – Ho1 – O6^a	64.6(4)
O3B^a – Ho1 – O5^a	49.8(3)
O3B^a – Mo1 – O3A	78.0(4)

O3A - Ho1 - O1	115.7(3)
O3A - Ho1 - O2	148.4(4)
O3A - Ho1 - O5	47.6(3)
O3A - Ho1 - O1^a	75.4(3)
O3A - Ho1 - O2^a	83.2(4)
O3A - Ho1 - O5^a	81.2(4)
O3A - Ho1 - O6^a	142.6(5)
O2- Ho1 - O1	74.4(2)
O2 - Ho1 - O5^a	105.7(2)
O1 - Ho1 - O5^a	148.5(2)
O2 - Ho1 - O1^a	77.4(2)
O1^a - Ho1 - O1	135.4(2)
O5^a - Ho1 - O1^a	72.7(2)
O2 - Ho1 - O6^a	67.6(3)
O1 - Ho1 - O6^a	75.5(3)
O5^a- Ho1 - O6^a	75.7(4)
O1^a- Ho1 - O6^a	123.4(3)
O2 - Ho1 -O2^a	70.4(3)
O1 - Ho1 - O2^a	74.5(2)
O5^a- Ho1 - O2^a	136.1(3)
O1^a- Ho1 - O2^a	63.7(2)
O6^a- Ho1 - O2^a	133.3(3)
O2 - Ho1 - O5	143.9(2)
O1 - Ho1 - O5	71.9(2)
O5 - Ho1 - O5^a	109.7(3)

O1^a - Ho1 - O5	119.6(2)
O6^a - Ho1 - O5	115.2(5)
O2^a - Ho1 - O5	88.4(2)
Cu1 - O1 - Ho1	100.3(2)
Cu1 - O2 - Ho1	98.6(2)
Cu1^a - O1^a-Ho1	103.8(2)
Cu1^a – O2^a – Ho1	97.5(2)

Data collection methods were the same as those for complexes 1-4. 15287 reflection data were collected of which 8624 unique and 5486 had $I>2\sigma(I)$. The structure was determined by direct methods using Shelxl97 and refined with Shelx2016-6 to R1 and wR2 values on observed data of 0.1022, 0.2387 and all data of 0.1385, 0.2576. Many attempts were made torefine the light atoms anisotropically and/or impose disordered models but none proved successful. So here we report the results from a refinement in which only the Er and Cu atoms were refined anisotropically together with isotropicrefinement of the remaining atoms.

The ORTEP view of complex **5** with thermal ellipsoids is depicted in Fig. 3 and shows a trinuclear $[(Cu^{II}L)_2Er^{III}]$ unit. As in the other four complexes, two Cu^{II} metalloligands of ligand $[L^{2-}]$ coordinate to the central Er^{III} atom *via* four μ_2-phenoxido bridged oxygen atoms in a *cisoid* fashion but unlike the other structures, there are no additional donor atoms in the coordination sphere. The angle between the two terminal

Cu^{II} atoms with the central Er^{III} atom is 85.00(1)° which is slightly higher than that observed in complex **4**. Besides the two metalloligands, two nitrato ligands coordinate to the Er^{III} atom in chelating bidentate (*κ2O,O′*) mode to complete the eight-coordination around the central Er^{III} atom.

The geometry around the erbium is best considered as a square antiprism. The Er−O bond distances of four phenoxido oxygens (O1, O2,O3 and O4) are in the range 2.16(2)−2.33(2)Å, much shorter than those involving the four nitrato oxygens (O6, O7, O9 and O10) are in the range of 2.39(3)−2.51(3) Å.It is also to be noted that, in both molecules (**4** and **5**) Ln–O1 (O1 is phenoxido oxygen of *o*-hydroxyacetophenone) distance is shorter than the Ln–O2 (O2 is phenoxido oxygen of salicylaldehyde) distance. The two terminal Cu^{II} atoms of this complex are coordinated to the same ligand [L^{2-}], but the geometry of these atoms are different. In equatorial plane both the Cu^{II} atoms are coordinated by four donor atoms of the ligand. Cu1 is coordinated to O1, O2, N1and N2, whereas Cu2 is coordinated to O3, O4, N4 and N5. One of the axial positions of Cu1 is occupied by N3 atom of a coordinated acetonitrile. But in the case of Cu2, two oxygen atoms of a nitrato group coordinate to one of its axial position with a small bite angle (O12–Cu2–O13) of 53.9(11)°. In the equatorial planes the Cu−O and Cu−N distances around the two Cu^{II} atoms are in the ranges of 1.89(2)−1.98(2)Å and 1.95(3)−2.04(3) Å, respectively. The axial Cu1−N3 distance is 2.48(3) Å and the two Cu2−O13and Cu2-O12 distances are 2.25(4), 2.60(4) Å respectively. In the equatorial plane the r.m.s. deviation of the four donor atoms O1, O2, N1 and N2 is 0.241 Å, where the Cu1 atom is shifted from the mean plane by 0.191Å towards the N3 atom. The r.m.s. deviation of O3, O4, N4 and N5 from the equatorial plane is 0.285Å. Here the Cu2 atom is deviated from the mean plane by 0.453Å towards the O12 and O13 atoms. The deviation of the Cu2 atom from the mean plane is more than that of the Cu1atom. The geometry of two Cu^{II} atoms (Cu1 and Cu2) is best considered as distorted square pyramidal with τ values[16] of 0.345 and 0.562 respectively. Distortion from this geometry is more in case of Cu2 atom than the Cu1atom.

Table S3. Crystal Data for **5.**

Compound **5**, $C_{39}H_{40}Cu_2ErN_{8.5}O_{13}$, M = 1130.64, monoclinic, space group *Cc*, $a = 10.212(5)$, $b = 20.369(5)$, $c = 23.068(5)$ Å, $\beta = 100.324(5)^{o}$, V = 4721(3)Å, dcalc = 1.591 gcm^{-3}.

Dimensions (distances, Å, angles, deg) in the coordination sphere of **5.**

Cu1 - O1	1.89(2)
Cu1 - O2	1.98(2)
Cu1 - N1	1.99(3)
Cu1 - N2	2.02(3)
Cu1 - N3	2.48(3)

Cu2 - N4	1.95(4)
Cu2 - O4	1.98(2)
Cu2 - O3	2.00(2)
Cu2 - N5	2.04(3)
Cu2 - O13	2.25(4)

Er1 - O3	2.16(2)
Er1 - O1	2.30(2)
Er1 - O2	2.30(2)
Er1 - O4	2.33(2)
Er1 - O10	2.39(3)
Er1 - O9	2.43(3)
Er1 - O6	2.45(3)
Er1 - O7	2.51(3)

O1 - Cu1 - O2	84.3(8)
O1 - Cu1 - N1	89.1(10)
O2 - Cu1 - N1	153.7(10)
O1 - Cu1 - N2	174.0(10)
O2 - Cu1 - N2	91.4(10)
N1 - Cu1 - N2	96.6(11)
O1 - Cu1 - N3	89.4(13)
O2 - Cu1 - N3	102.4(13)
N1 - Cu1 - N3	102.9(13)
N2 - Cu1 - N3	87.4(13)

N4 - Cu2 - O3	89.4(13)
O4 - Cu2 - O3	82.5(9)
N4 - Cu2 - N5	91.3(14)
O4 - Cu2 - N5	89.7(10)
O3 - Cu2 - N5	169.7(11)
N4 - Cu2 - O13	139.0(14)
O4 - Cu2 - O13	85.3(11)
O3 - Cu2 - O13	90.8(11)
N5 - Cu2 - O13	95.4(12)

O3 - Er1 - O1	144.0(8)
O3 - Er1 - O2	84.4(8)
O1 - Er1 - O2	68.9(7)
O3 - Er1 - O4	71.5(8)
O1 - Er1 - O4	81.8(7)
O2 - Er1 - O4	83.9(7)
O3 - Er1 - O10	131.4(9)
O1 - Er1 - O10	78.1(8)
O2 - Er1 - O10	144.2(8)
O4 - Er1 - O10	105.0(8)
O3 - Er1 - O9	81.6(9)
O1 - Er1 - O9	119.8(7)

O2 - Er1 - O9	163.9(8)
O4 - Er1 - O9	84.2(8)
O10 - Er1 - O9	50.2(9)
O3 - Er1 - O6	78.6(9)
O1 - Er1 - O6	129.9(9)
O2 - Er1 - O6	103.8(8)
O4 - Er1 - O6	148.3(9)
O10 - Er1 - O6	86.8(9)
O9 - Er1 - O6	81.2(9)
O3 - Er1 - O7	121.0(8)
O1 - Er1 - O7	79.2(8)
O2 - Er1 - O7	80.9(8)
O4 - Er1 - O7	159.0(7)
O10 - Er1 - O7	79.8(9)
O9 - Er1 - O7	113.2(9)
O6 - Er1 - O7	51.0(9)

Cu1 – O1 - Er1	101.2(1)
Cu1 – O2 – Er1	98.3(1)
Cu2 – O3 – Er1	104.1(1)
Cu2 – O4 – Er1	99.3(1)