Supplementary Materials: Key Role of the Size and Electronic Configuration on the Sign and Strength of the Magnetic Coupling in a Series of Cu_2Ln Trimers (Ln = Ce, Gd, Tb, Dy and Er)

Soumavo Ghosh, Carlos J. Gómez García, Juan M. Clemente-Juan and Ashutosh Ghosh

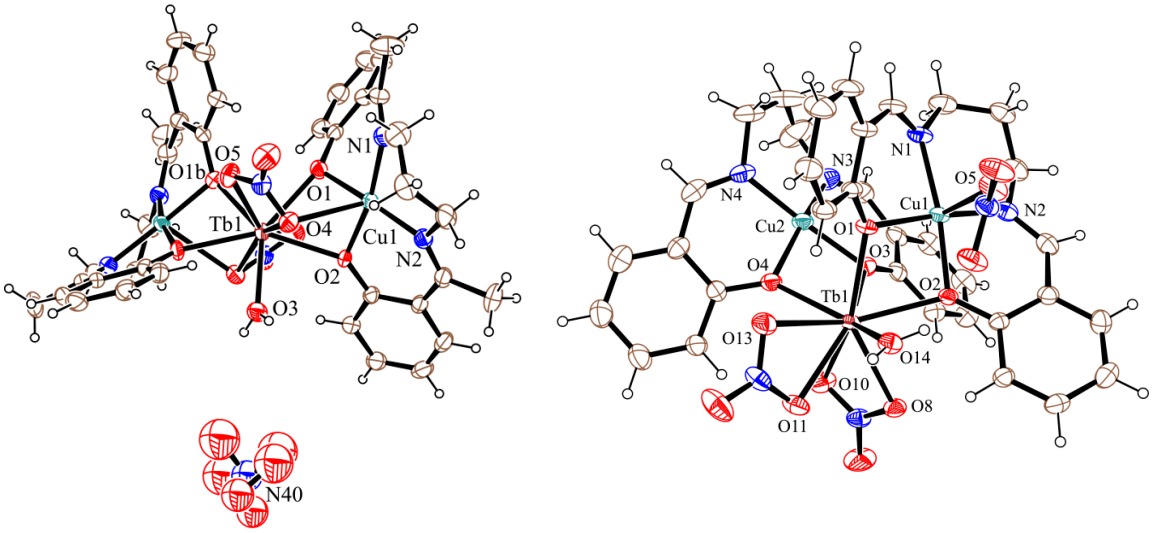

Figure S1. ORTEP diagram of the *transoid* complex **3** at 30 % probability (**left**) along with the ORTEP diagram at 30% probability of a previously reported *cisoid* complex derived from [CuL^3] (**right**). The Cu(1)-Cu(1a) distance is 6.435(2)Å in the *transoid* complex **3** whereas the Cu(1)-Cu(2) distance is 3.736(1)Å in the *cisoid* Cu-Tb complex.

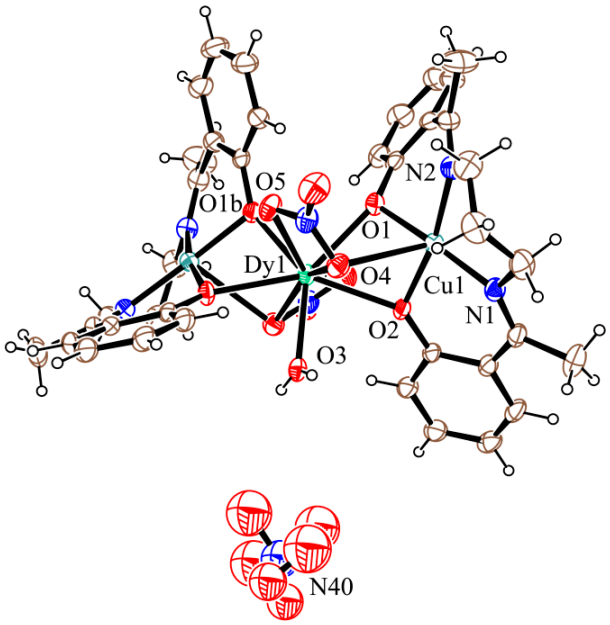

Figure S2. ORTEP diagram of complex **4** at 30% probability.

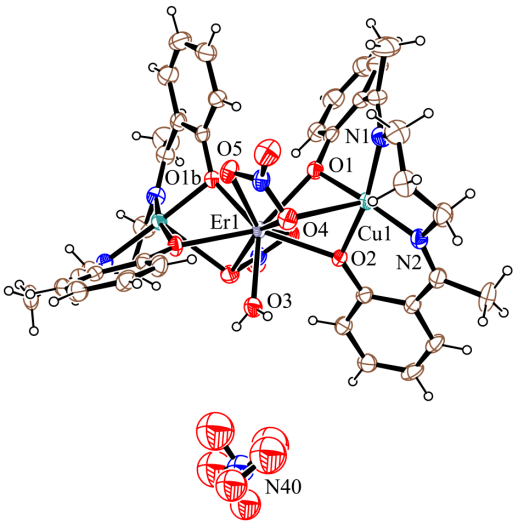

Figure S3. ORTEP diagram of complex **5** at 30% probability.

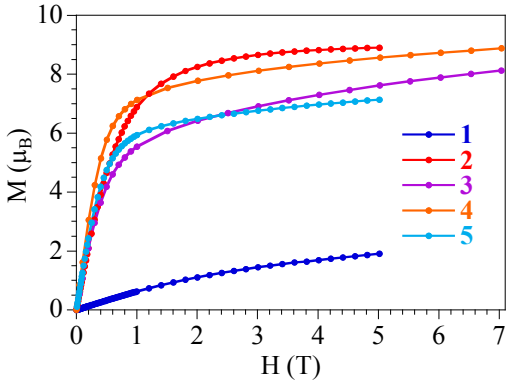

Figure S4. Isothermal magnetizations at 2 K for compounds **1–5** (per Cu_2Ln unit). Solid lines are guides for the eyes.

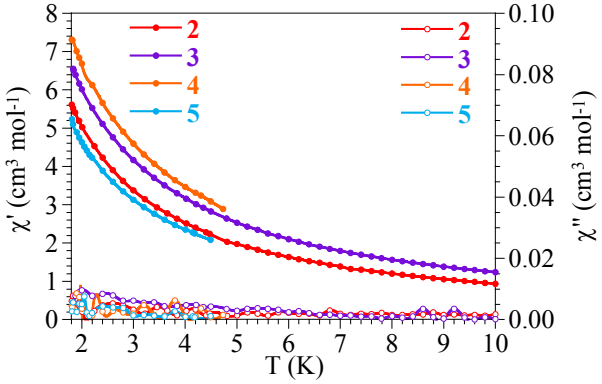

Figure S5. Thermal variation of the in phase (χ_m', filled symbols, left scale) and out of phase (χ_m'', empty symbols, right scale) AC susceptibilities for compounds **2–5**.

Table S1. Bond distances (Å)around the metal centers in complexes **1** to **5**.

Bonds	**1** (Å)	**2** (Å)	**3** (Å)	**4** (Å)	**5** (Å)
Cu(1)-O(1)	1.901(3)	1.964(5)	1.973(4)	1.975(4)	1.979(3)
Cu(1)-O(2)	1.932(2)	1.881(6)	1.898(4)	1.900(5)	1.900(3)
Cu(1)-N(1)	1.953(4)	1.943(7)	1.964(5)	1.967(6)	1.953(4)
Cu(1)-N(2)	1.953(5)	1.936(7)	1.945(5)	1.952(5)	1.955(5)
Cu(1)-O(13)/O(4)	2.709(4)	2.598(6)	2.614(5)	2.599(5)	2.587(4)
Cu(2)-O(3)	1.940(3)	-	-	-	-
Cu(2)-O(4)	1.912(2)	-	-	-	-
Cu(2)-N(3)	1.959(3)	-	-	-	-
Cu(2)-N(4)	1.949(3)	-	-	-	-
Cu(2)-O(7)	2.489(3)	-	-	-	-
Ln(1)-O(1)	2.612(3)	2.360(5)	2.347(4)	2.336(4)	2.309(3)
Ln(1)-O(2)	2.431(2)	2.409(5)	2.418(4)	2.410(5)	2.401(3)
Ln(1)-O(3)	2.464(2)	2.351(10)	2.336(6)	2.357(8)	2.312(6)
Ln(1)-O(4)	2.582(2)	2.499(6)	2.519(5)	2.505(5)	2.488(4)
Ln(1)-O(5)	2.641(3)	2.477(6)	2.478(4)	2.474(5)	2.458(3)
Ln(1)-O(7)	2.614(3)	-	-	-	-
Ln(1)-O(8)	2.602(3)	-	-	-	-
Ln(1)-O(10)	2.561(3)	-	-	-	-
Ln(1)-O(11)	2.608(3)	-	-	-	-
Ln(1)-O(13)	2.649(4)	-	-	-	-
Cu(1)-Ln(1)	3.417(1)	3.255(1)	3.268(1)	3.259(1)	3.242(1)
Cu(2)-Ln(1)	3.380(1)	-	-	-	-
Cu(1)-Cu(2)/Cu(1 [a])	6.313(1)	6.410(2)	6.435(2)	6.418(2)	6.388(2)

Ln = Ce for **1**, Gd for **2**, Tb for **3**, Dy for **4** and Er for **5**. O(13) for **1** and O(4) for **2**-**5**. Symmetry code "a" = 1−*x*,*y*,3/2−*z* for complexes **2**–**5**.

Table S2. Bond angles (º) around the metal centers in complex **1**.

Atoms	**Angle**	**Atoms**	**Angle**
O(1)-Cu(1)-O(2)	85.35(11)	O(2)-Ce(1)-O(7)	99.62(9)
O(1)-Cu(1)-N(1)	93.98(14)	O(2)-Ce(1)-O(8)	142.02(9)
O(1)-Cu(1)-N(2)	160.85(15)	O(2)-Ce(1)-O(10)	134.43(9)
O(1)-Cu(1)-O(13)	72.47(11)	O(2)-Ce(1)-O(11)	101.01(9)
O(2)-Cu(1)-N(1)	171.47(14)	O(2)-Ce(1)-O(13)	72.24(10)
O(2)-Cu(1)-N(2)	88.67(15)	O(3)-Ce(1)-O(4)	60.79(7)
O(2)-Cu(1)-O(13)	78.57(11)	O(3)-Ce(1)-O(5)	101.25(10)
N(1)-Cu(1)-N(2)	94.56(17)	O(3)-Ce(1)-O(7)	70.59(9)
N(1)-Cu(1)-O(13)	109.37(14)	O(3)-Ce(1)-O(8)	128.41(9)
N(2)-Cu(1)-O(13)	88.53(15)	O(3)-Ce(1)-O(10)	142.03(9)
		O(3)-Ce(1)-O(11)	75.62(9)
O(3)-Cu(2)-O(4)	83.08(10)	O(3)-Ce(1)-O(13)	103.30(10)
O(3)-Cu(2)-N(3)	88.90(12)	O(4)-Ce(1)-O(5)	110.71(9)
O(3)-Cu(2)-N(4)	170.47(12)	O(4)-Ce(1)-O(7)	64.35(8)
O(3)-Cu(2)-O(7)	82.06(10)	O(4)-Ce(1)-O(8)	73.98(9)
O(4)-Cu(2)-N(3)	166.96(11)	O(4)-Ce(1)-O(10)	87.69(8)
O(4)-Cu(2)-N(4)	90.97(11)	O(4)-Ce(1)-O(11)	71.50(9)
O(4)-Cu(2)-O(7)	76.66(10)	O(4)-Ce(1)-O(13)	118.84(10)
N(3)-Cu(2)-N(4)	98.24(13)	O(5)-Ce(1)-O(7)	47.45(9)
N(3)-Cu(2)-O(7)	92.10(12)	O(5)-Ce(1)-O(8)	71.68(11)

Table S2. *Cont.*

Atoms	Angle	Atoms	Angle
N(4)-Cu(2)-O(7)	103.86(11)	O(5)-Ce(1)-O(10)	109.99(11)
		O(5)-Ce(1)-O(11)	174.88(10)
O(1)-Ce(1)-O(2)	61.89(8)	O(5)-Ce(1)-O(13)	130.44(11)
O(1)-Ce(1)-O(3)	136.08(8)	O(7)-Ce(1)-O(8)	68.26(10)
O(1)-Ce(1)-O(4)	163.01(8)	O(7)-Ce(1)-O(10)	116.47(11)
O(1)-Ce(1)-O(5)	68.01(9)	O(7)-Ce(1)-O(11)	133.40(9)
O(1)-Ce(1)-O(7)	115.27(9)	O(7)-Ce(1)-O(13)	171.18(11)
O(1)-Ce(1)-O(8)	89.97(9)	O(8)-Ce(1)-O(10)	48.97(11)
O(1)-Ce(1)-O(10)	77.37(9)	O(8)-Ce(1)-O(11)	113.44(10)
O(1)-Ce(1)-O(11)	111.32(9)	O(8)-Ce(1)-O(13)	120.22(11)
O(1)-Ce(1)-O(13)	64.37(11)	O(10)-Ce(1)-O(11)	74.47(10)
O(2)-Ce(1)-O(3)	74.19(8)	O(10)-Ce(1)-O(13)	72.30(11)
O(2)-Ce(1)-O(4)	134.90(7)	O(11)-Ce(1)-O(13)	47.70(11)
O(2)-Ce(1)-O(5)	74.11(10)	Cu(1)-Ce(1)-Cu(2)	136.50(1)

Table S3. Bond angles (º) around the metal centers in complexes **2**–**5**.

Atoms	2	3	4	5
O(1)-Cu(1)-O(2)	84.0(2)	83.67(15)	83.39(18)	83.25(14)
O(1)-Cu(1)-N(1)	87.4(3)	87.54(19)	87.83(19)	87.85(17)
O(1)-Cu(1)-N(2)	173.1(3)	173.12(17)	172.9(2)	172.33(16)
O(1)-Cu(1)-O(4)	77.9(2)	77.13(14)	77.40(17)	77.05(12)
O(2)-Cu(1)-N(1)	169.2(3)	169.12(19)	169.3(2)	168.96(17)
O(2)-Cu(1)-N(2)	91.2(3)	91.31(19)	91.2(2)	90.71(17)
O(2)-Cu(1)-O(4)	74.3(2)	74.75(16)	74.51(18)	74.36(13)
N(1)-Cu(1)-N(2)	97.9(3)	98.0(2)	98.0(2)	98.67(19)
N(1)-Cu(1)-O(4)	97.5(3)	97.08(17)	97.7(2)	97.33(16)
N(2)-Cu(1)-O(4)	105.7(3)	106.12(18)	105.6(2)	105.92(15)
O(1)-Ln(1)-O(1 [a])	86.36(18)	86.48(12)	86.25(13)	85.86(11)
O(1)-Ln(1)-O(2)	65.33(18)	65.62(12)	65.78(13)	66.31(11)
O(1)-Ln(1)-O(2 [a])	144.05(18)	144.11(13)	143.93(14)	144.02(11)
O(1)-Ln(1)-O(3)	136.82(13)	136.76(9)	136.88(9)	137.07(8)
O(1)-Ln(1)-O(4)	73.53(18)	73.18(12)	73.53(16)	73.81(12)
O(1)-Ln(1)-O(4 [a])	126.05(18)	125.83(12)	126.29(16)	126.35(12)
O(1)-Ln(1)-O(5)	76.09(18)	76.27(13)	76.06(16)	76.55(11)
O(1)-Ln(1)-O(5 [a])	75.76(18)	76.29(13)	76.30(16)	76.02(11)
O(2)-Ln(1)-O(2 [a])	148.81(19)	148.35(13)	148.35(13)	147.70(12)
O(2)-Ln(1)-O(3)	74.41(14)	74.17(9)	74.18(9)	73.85(8)
O(2)-Ln(1)-O(4)	68.5(2)	68.99(15)	68.85(15)	68.90(12)
O(2)-Ln(1)-O(4 [a])	104.71(19)	104.35(14)	104.22(15)	103.94(12)
O(2)-Ln(1)-O(5)	115.2(2)	115.36(15)	115.73(16)	116.10(11)
O(2)-Ln(1)-O(5 [a])	75.8(2)	75.49(15)	75.19(16)	74.94(11)
O(3)-Ln(1)-O(4)	77.94(13)	78.28(9)	77.80(13)	77.63(9)
O(3)-Ln(1)-O(5)	109.48(13)	109.00(9)	109.11(13)	108.90(9)
O(4)-Ln(1)-O(4 [a])	155.87(19)	156.56(13)	155.61(19)	155.25(13)
O(4)-Ln(1)-O(5)	51.2(2)	50.51(15)	51.19(17)	51.35(12)
O(4)-Ln(1)-O(5 [a])	140.0(2)	140.19(16)	139.92(16)	139.77(12)
O(5)-Ln(1)-O(5 [a])	141.04(19)	142.00(13)	141.78(19)	142.21(13)
Cu(1)-Ln(1)-Cu(1 [a])	159.78(4)	159.87(2)	159.94(2)	160.15(2)

Ln = Gd for **2**, Tb for **3**, Dy for **4** and Er for **5**. symmetry code "a" = 1−*x*,*y*,3/2−*z* for complexes **2**–**5**.