Supporting Information for the Manuscript:

Compartmental Ligand Approach for Constructing 3d−4f Heterometallic $[Cu^{II}_5Ln^{III}_2]$ Clusters: Synthesis and Magnetostructural Properties

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Supplementary Information Contents:

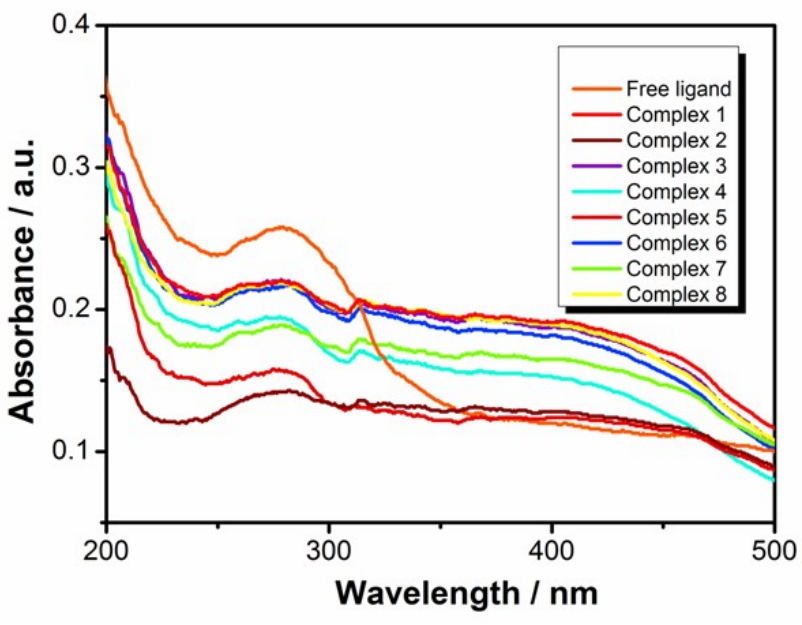

Figure S1 UV–Vis reflectance spectra of free ligand and complexes **1**-**8** in $BaSO_4$ after Kubelka–Munk transformation.

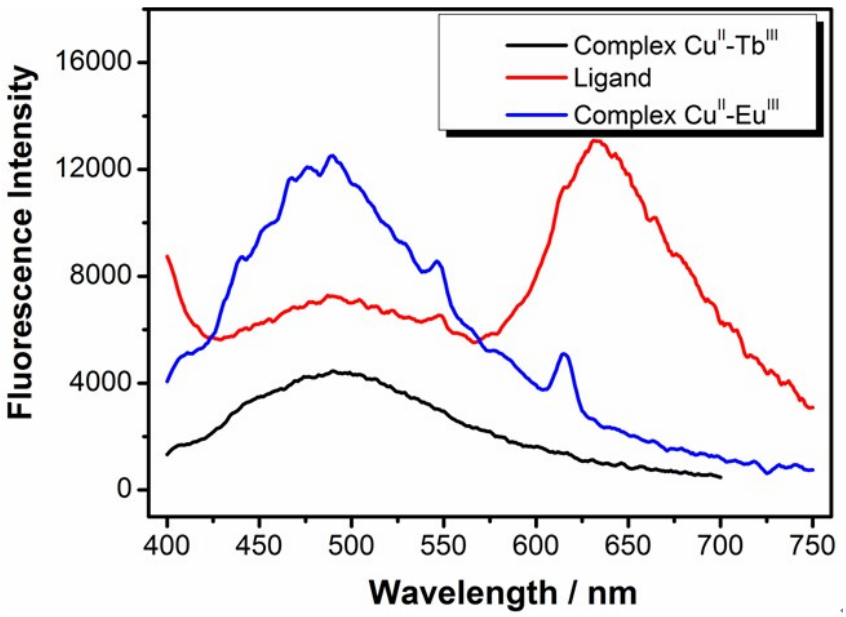

Figure S2 Luminescence spectrum of free ligand and complexes **2** and **4** in solid state at 298 K, λ_{exc}= 306, 306 and 356 nm, respectively.

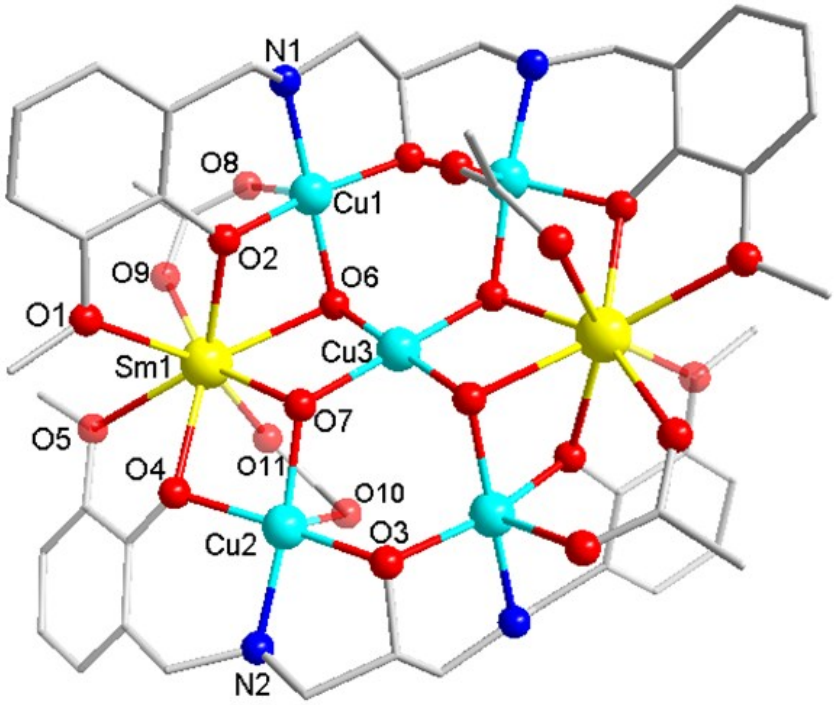

Figure S3 Molecular structure of complex **1**. Solvent molecules, PF_6^{-1} ion and H atoms are omitted for clarity.

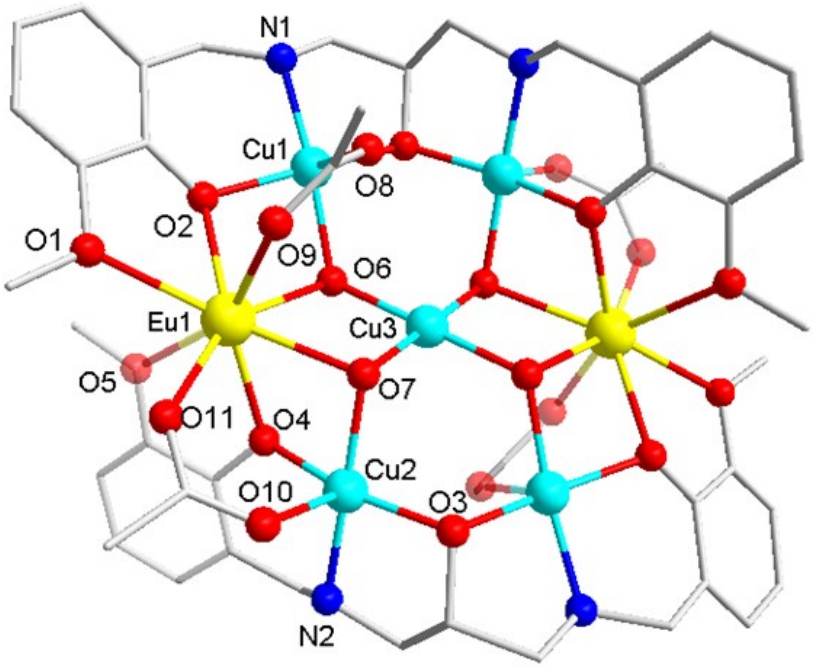

Figure S4 Molecular structure of complex **2**. Solvent molecules, PF_6^{-1} ion and H atoms are omitted for clarity.

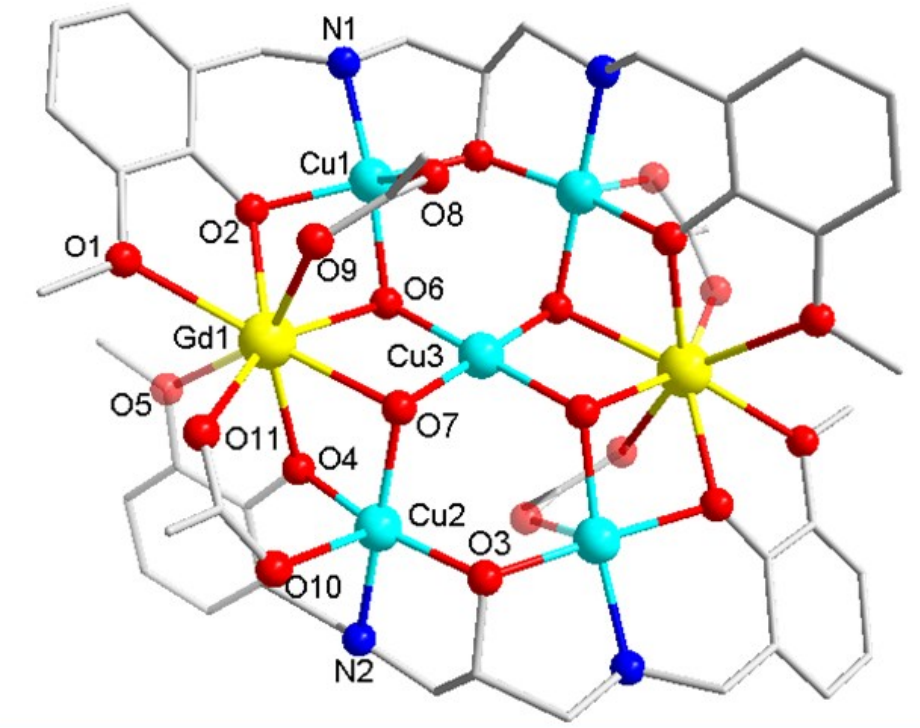

Figure S5 Molecular structure of complex **3**. Solvent molecules, NO_3^{-1} ions and H atoms are omitted for clarity.

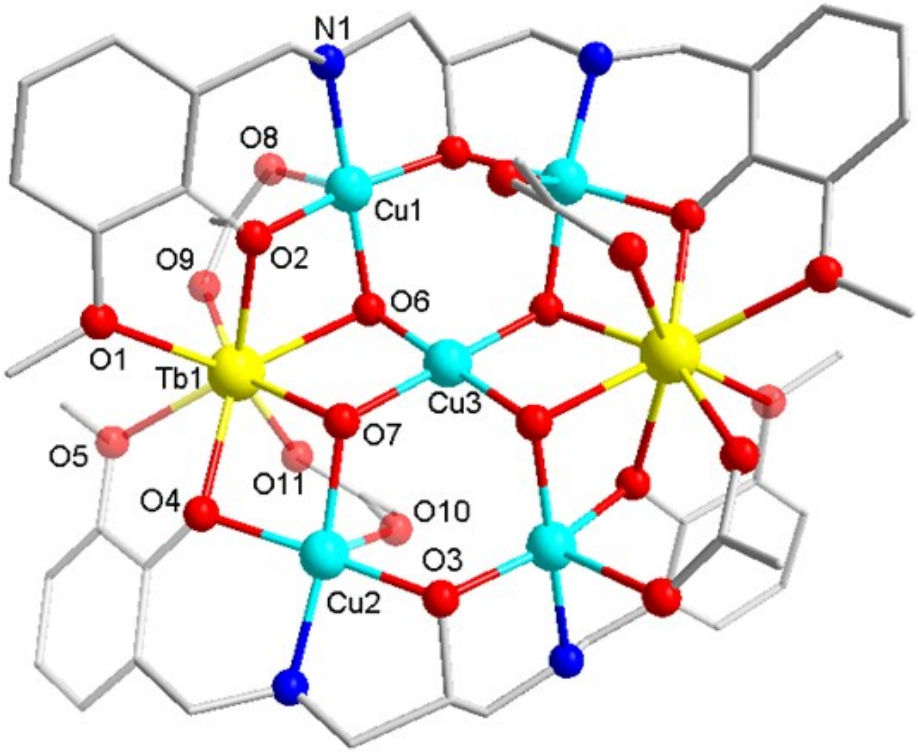

Figure S6 Molecular structure of complex **4**. Solvent molecules, NO_3^{-1} ions and H atoms are

omitted for clarity.

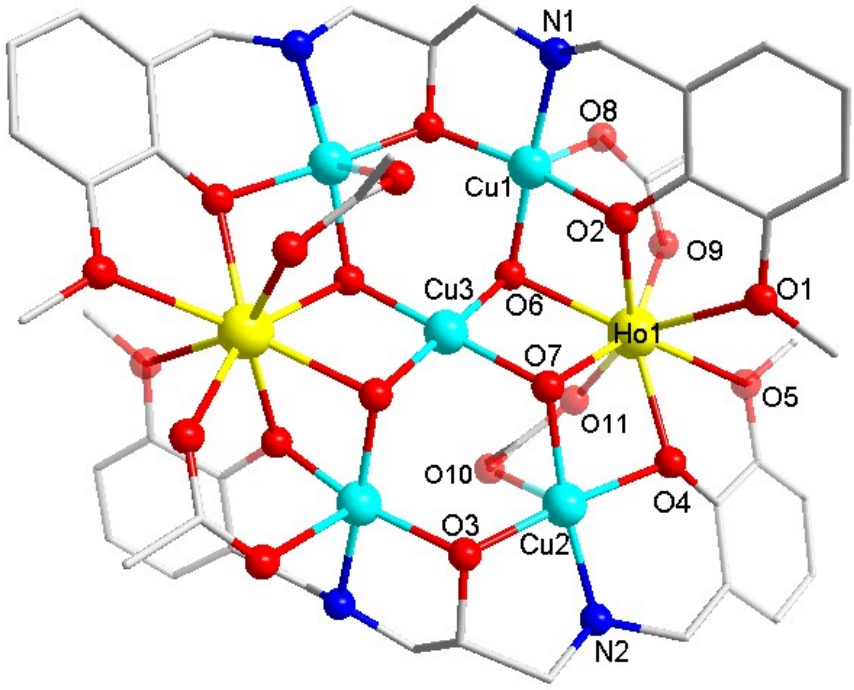

Figure S7 Molecular structure of complex **6**. Solvent molecules, NO_3^{-1} ions and H atoms are omitted for clarity.

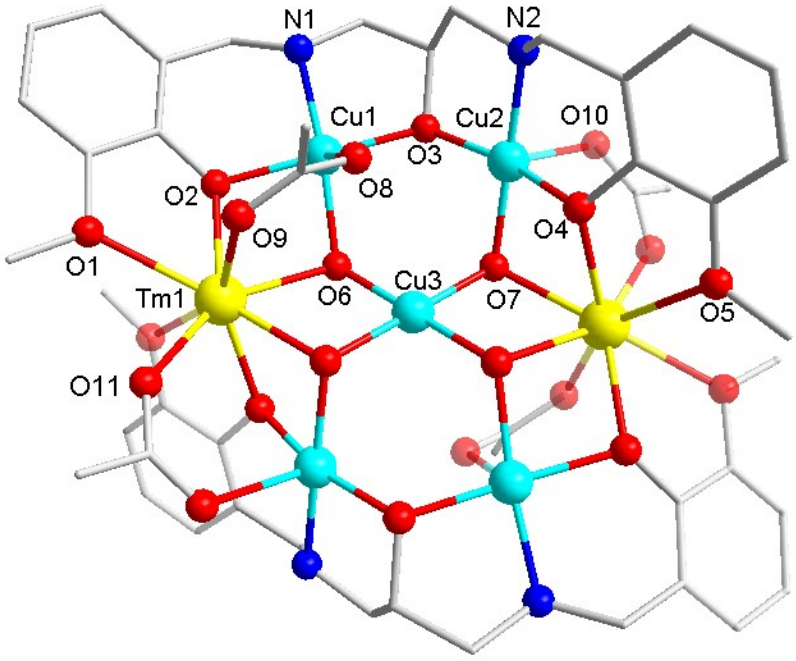

Figure S8 Molecular structure of complex **7**. Solvent molecules, NO_3^{-1} ions and H atoms are

omitted for clarity.

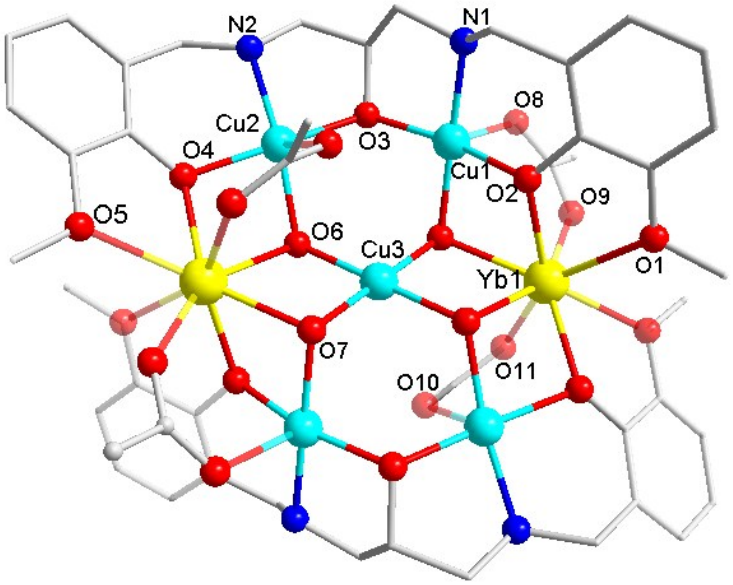

Figure S9 Molecular structure of complex **8**. Solvent molecules, NO_3^{-1} ions and H atoms are omitted for clarity.

Table S1 Selected coordination bond distances (Å) for **1-4**.

1		**2**		**3**		**4**	
Selected bond distances around copper							
Cu3-O6[1]	1.924(3)	Cu2-O3	1.931(3)	Cu2-O7	1.960(3)	Cu2-O3	1.938(5)
Cu3-O6	1.924(3)	Cu2-O7	1.979(3)	Cu2-O3	1.936(3)	Cu2-O7	1.999(5)
Cu3-O7	1.953(3)	Cu2-O4	1.951(3)	Cu2-O4	1.956(3)	Cu2-O4	1.986(5)
Cu3-O7[1]	1.953(3)	Cu2-N2	1.981(3)	Cu2-O10	2.310(3)	Cu2-N2	1.996(5)
Cu2-O3	1.953(3)	Cu2-O10	2.263(3)	Cu2-N2	1.986(4)	Cu2-O10	2.284(6)
Cu2-O4	1.987(3)	Cu3-O7[1]	1.930(3)	Cu3-O7	1.919(3)	Cu3-O6	1.921(4)
Cu2-O7	1.992(3)	Cu3-O7	1.930(3)	Cu3-O7[1]	1.919(3)	Cu3-O6[1]	1.921(4)
Cu2-O10	2.216(3)	Cu3-O6[1]	1.947(3)	Cu3-O6[1]	1.967(3)	Cu3-O7[1]	1.967(4)
Cu2-N2	1.996(4)	Cu3-O6	1.947(3)	Cu3-O6	1.967(3)	Cu3-O7	1.967(4)
Cu1-O6	1.977(3)	Cu1-O3[1]	1.957(3)	Cu1-O6	2.000(3)	Cu1-O6	1.964(5)
Cu1-O3[1]	1.940(3)	Cu1-O6	1.996(3)	Cu1-O3[1]	1.941(3)	Cu1-O3[1]	1.928(5)
Cu1-O2	1.956(3)	Cu1-N1	1.999(3)	Cu1-O2	2.001(3)	Cu1-N1	1.987(6)
Cu1-O8	2.270(3)	Cu1-O8	2.225(3)	Cu1-N1	1.993(4)	Cu1-O2	1.949(4)
Cu1-N1	1.986(4)	Cu1-O2	1.981(3)	Cu1-O8	2.288(4)	Cu1-O8	2.295(5)
				O3-Cu1[1]	1.941(3)	O3-Cu1[1]	1.928(5)
Selected bond distances around samarium		Selected bond distances around europium		Selected bond distances around gadolinium		Selected bond distances around terbium	
Sm1-O6	2.437(3)	Eu1-O7	2.423(3)	Gd1-O7	2.360(3)	Tb1-O6	2.341(4)
Sm1-O4	2.383(3)	Eu1-O6	2.401(3)	Gd1-O6	2.411(3)	Tb1-O7	2.396(5)

Sm1-O7	2.405(3)	Eu1-O5	2.519(3)	Gd1-O2	2.363(3)	Tb1-O4	2.343(4)
Sm1-O2	2.375(3)	Eu1-O1	2.525(3)	Gd1-O1	2.511(3)	Tb1-O5	2.504(5)
Sm1-O5	2.531(3)	Eu1-O4	2.364(3)	Gd1-O4	2.361(3)	Tb1-O2	2.350(5)
Sm1-O1	2.530(3)	Eu1-O9	2.325(3)	Gd1-O9	2.315(3)	Tb1-O1	2.536(5)
Sm1-O9	2.309(3)	Eu1-O2	2.380(3)	Gd1-O5	2.557(3)	Tb1-O9	2.284(5)
Sm1-O11	2.344(3)	Eu1-O11	2.300(3)	Gd1-O11	2.300(3)	Tb1-O11	2.300(5)
[1]1-X,2-Y,1-Z		[1]1-X,1-Y,1-Z		[1]2-X,2-Y,2-Z		[1]2-X,1-Y,2-Z	

Table S2 Selected coordination bond distances (Å) for **5-8**.

5		**6**		**7**		**8**	
Selected bond distances around copper							
Cu3-O6	1.923(5)	Cu3-O6[1]	1.947(4)	Cu3-O6	1.959(4)	Cu3-O7[1]	1.936(3)
Cu3-O6[1]	1.923(5)	Cu3-O6	1.947(4)	Cu3-O61	1.959(4)	Cu3-O7	1.936(3)
Cu3-O7[1]	1.962(5)	Cu3-O7	1.982(4)	Cu3-O71	1.925(5)	Cu3-O6	1.976(4)
Cu3-O7	1.962(5)	Cu3-O7[1]	1.982(4)	Cu3-O7	1.925(5)	Cu3-O6[1]	1.976(4)
Cu2-O4	1.992(5)	Cu2-O7	1.999(4)	Cu2-O7	1.939(6)	Cu3-O10	2.987(8)
Cu2-O7	1.994(5)	Cu2-O3	1.962(4)	Cu2-O3	1.932(4)	Cu1-O7[1]	1.961(4)
Cu2-O3	1.943(5)	Cu2-N2	2.008(4)	Cu2-O4	1.951(5)	Cu1-O2	1.956(4)
Cu2-N1	1.987(5)	Cu2-O4	1.994(4)	Cu2-O10	2.309(5)	Cu1-O3	1.944(4)
Cu2-O10	2.302(6)	Cu2-O10	2.301(5)	Cu2-N2	1.976(6)	Cu1-O8	2.311(5)
Cu1-O6	1.955(5)	Cu1-O6	1.958(4)	Cu1-O6	2.003(5)	Cu1-N1	1.991(5)
Cu1-O3[1]	1.931(5)	Cu1-O3[1]	1.956(4)	Cu1-O3	1.959(5)	Cu2-O6	1.993(4)
Cu1-O2	1.947(4)	Cu1-O2	1.977(4)	Cu1-O2	1.994(5)	Cu2-O4	1.995(4)
Cu1-N2	1.997(6)	Cu1-O8	2.313(4)	Cu1-N1	1.989(6)	Cu2-O3	1.948(4)
Cu1-O8	2.298(5)	Cu1-N1	1.997(5)	Cu1-O8	2.359(6)	Cu2-N2	1.993(5)
O3-Cu1[1]	1.931(5)	O3-Cu1[1]	1.956(4)			Cu2-O10[1]	2.353(6)
Selected bond distances around samarium		Selected bond distances around holmium		Selected bond distances around thulium		Selected bond distances around ytterbium	
Dy1-O6	2.338(4)	Ho1-O6	2.349(4)	Tm1-O6	2.356(5)	Yb1-O7[1]	2.309(4)
Dy1-O11	2.283(5)	Ho1-O7	2.375(4)	Tm1-O7[1]	2.311(5)	Yb1-O6[1]	2.354(4)
Dy1-O4	2.338(4)	Ho1-O4	2.332(4)	Tm1-O2	2.301(5)	Yb1-O4[1]	2.295(4)
Dy1-O7	2.394(5)	Ho1-O2	2.341(4)	Tm1-O9	2.244(5)	Yb1-O2	2.298(4)
Dy1-O5	2.500(4)	Ho1-O5	2.529(4)	Tm1-O4[1]	2.298(5)	Yb1-O11	2.242(4)
Dy1-O2	2.338(4)	Ho1-O9	2.270(4)	Tm1-O1	2.500(5)	Yb1-O1	2.520(4)
Dy1-O1	2.538(5)	Ho1-O11	2.310(4)	Tm1-O5[1]	2.528(5)	Yb1-O9	2.222(4)
Dy1-O9	2.271(5)	Ho1-O1	2.505(4)	Tm1-O11	2.217(5)	Yb1-O5[1]	2.501(4)
				O7-Tm1[1]	2.311(5)	O7-Yb1[1]	2.309(4)
				O4-Tm1[1]	2.298(5)	O6-Yb1[1]	2.354(4)
						O4-Yb1[1]	2.295(4)
						O5-Yb1[1]	2.501(4)
[1]-X,1-Y,1-Z		[1]1-X,2-Y,-Z		[1]-X,2-Y,1-Z		[1]2-X,-Y,1-Z	

Table S3 Selected coordination bond angles (°) for **1-4**.

1		**2**		**3**		**4**	
Bond angles containing both samarium and copper		Bond angles containing both europium and copper		Bond angles containing both gadolinium and copper		Bond angles containing both terbium and copper	
Cu3[1]-O6-Sm1	102.13(13)	Cu2-O7-Eu1	99.89(12)	Cu2-O7-Gd1	101.37(14)	Cu3-O6-Tb1	103.28(17)
Cu1-O6-Sm1	99.84(13)	Cu3-O7-Eu1	101.98(12)	Cu3-O7-Gd1	103.60(14)	Cu3-O6-Cu1	109.1(2)
Cu1-O6-Cu31	108.30(15)	Cu3[1]-O6-Eu1	102.23(13)	Cu3-O7-Cu2	109.36(15)	Cu1-O6-Tb1	101.65(19)
Cu2-O4-Sm1	99.77(11)	Cu1-O6-Eu1	98.57(13)	Cu3-O6-Gd1	100.31(13)	Cu2-O7-Tb1	97.87(19)
Cu3-O7-Sm1	102.35(12)			Cu3-O6-Cu1	119.83(17)	Cu3-O7-Tb1	99.94(18)
Cu2-O7-Sm1	98.86(12)			Cu1-O6-Gd1	97.76(13)	Cu2-O4-Tb1	99.99(18)
Cu1-O2-Sm1	102.56(12)						
Bond angles around copper							
O6-Cu3-O61	180	O7-Cu2-O3	94.73(12)	O7-Cu2-O10	93.78(13)	O3-Cu2-O7	97.26(19)
O7-Cu3-O6	87.91(13)	O4-Cu2-O3	162.59(12)	O7-Cu2-N2	175.42(15)	O3-Cu2-O4	169.35(19)
O71-Cu3-O6	92.09(13)	O4-Cu2-O7	82.26(11)	O3-Cu2-O7	94.33(13)	O3-Cu2-N2	86.0(2)
O71-Cu3-O7	180	N2-Cu2-O3	87.90(12)	O3-Cu2-O4	165.57(13)	O3-Cu2-O10	87.7(2)
O4-Cu2-O3	166.24(12)	N2-Cu2-O7	175.20(13)	O3-Cu2-O10	97.80(13)	O7-Cu2-O10	87.1(2)
O11-Cu1-O2	83.19(11)	N2-Cu2-O4	94.04(12)	O3-Cu2-N2	87.80(14)	O4-Cu2-O7	81.86(19)
O7-Cu2-O3	95.95(12)	O10-Cu2-O3	98.29(11)	O4-Cu2-O7	82.71(13)	O4-Cu2-N2	93.1(2)
O7-Cu2-O4	83.07(11)	O10-Cu2-O7	91.73(11)	O4-Cu2-O10	96.49(13)	O4-Cu2-O10	102.8(2)
O10-Cu2-O3	94.47(12)	O10-Cu2-O4	98.94(11)	O4-Cu2-N2	94.23(14)	N2-Cu2-O7	169.4(2)
O10-Cu2-O4	99.23(12)	O10-Cu2-N2	91.87(12)	N2-Cu2-O10	89.93(14)	N2-Cu2-O10	103.2(3)
O10-Cu2-O7	89.02(13)	O7[1]-Cu3-O7	180	O7[1]-Cu3-O7	180.000(1)	O6-Cu3-O6[1]	180.000(1)
N2-Cu2-O3	85.76(13)	O6[1]-Cu3-O7	92.10(13)	O7[1]-Cu3-O6	92.88(14)	O6-Cu3-O7	87.18(19)
N2-Cu2-O4	93.42(13)	O6[1]-Cu3-O7[1]	87.90(13)	O7-Cu3-O6[1]	92.88(14)	O6-Cu3-O7[1]	92.82(19)
N2-Cu2-O7	172.06(14)	O6-Cu3-O7[1]	92.10(13)	O7[1]-Cu3-O6[1]	87.12(14)	O6[1]-Cu3-O7[1]	87.18(19)
N2-Cu2-O10	98.59(15)	O6-Cu3-O7	87.90(13)	O7-Cu3-O6	87.12(14)	O6[1]-Cu3-O7	92.82(19)
N1-Cu1-O6	175.32(15)	O6-Cu3-O6[1]	180	O61-Cu3-O6	180.000(1)	O7-Cu3-O7[1]	180.000(1)
N1-Cu1-O3[1]	87.68(13)	O6-Cu1-O3[1]	95.73(12)	O6-Cu1-O2	82.45(13)	O6-Cu1-N1	175.6(2)
N1-Cu1-O2	94.04(14)	N1-Cu1-O3[1]	86.12(12)	O6-Cu1-O8	86.42(16)	O6-Cu1-O8	94.02(19)
N1-Cu1-O8	91.84(13)	N1-Cu1-O6	171.93(13)	O3[1]-Cu1-O6	97.03(13)	O3[1]-Cu1-O6	94.43(18)
O31-Cu1-O6	94.72(13)	O8-Cu1-O3[1]	94.07(12)	O3[1]-Cu1-O2	168.98(13)	O3[1]-Cu1-N1	87.5(2)
O2-Cu1-O6	82.48(13)	O8-Cu1-O6	88.70(13)	O3[1]-Cu1-N1	86.10(14)	O3[1]-Cu1-O2	165.7(2)
O2-Cu1-O3[1]	162.59(12)	O8-Cu1-N1	99.02(13)	O3[1]-Cu1-O8	87.27(14)	O3[1]-Cu1-O8	97.58(18)
O8-Cu1-O6	91.78(12)	O2-Cu1-O3[1]	166.37(11)	O2-Cu1-O8	103.65(14)	N1-Cu1-O8	89.6(2)
O8-Cu1-O3[1]	98.43(11)	O2-Cu1-O6	83.20(11)	N1-Cu1-O6	169.53(15)	O2-Cu1-O6	82.26(18)
O8-Cu1-O2	98.82(12)	O2-Cu1-N1	93.15(12)	N1-Cu1-O2	92.56(14)	O2-Cu1-N1	94.9(2)

		O2-Cu1-O8	99.49(11)	N1-Cu1-O8	103.74(17)	O2-Cu1-O8	96.6(2)
Bond angles around samarium		Bond angles around europium		Bond angles around gadolinium		Bond angles around terbium	
O4-Sm1-O6	127.24(10)	O6-Eu1-O7	67.80(10)	O7-Gd1-O6	68.30(11)	O6-Tb1-O7	68.93(15)
O7-Sm1-O6	67.52(10)	O5-Eu1-O7	129.62(9)	O7-Gd1-O2	128.68(11)	O6-Tb1-O4	128.84(16)
O7-Sm1-O4	66.88(9)	O5-Eu1-O6	97.51(10)	O7-Gd1-O1	147.92(11)	O6-Tb1-O5	147.31(15)
O2-Sm1-O6	65.20(10)	O1-Eu1-O7	148.62(10)	O7-Gd1-O4	66.46(11)	O6-Tb1-O2	66.54(15)
O2-Sm1-O4	127.10(10)	O1-Eu1-O6	132.36(9)	O7-Gd1-O5	129.71(11)	O6-Tb1-O1	129.87(15)
O2-Sm1-O7	78.17(10)	O1-Eu1-O5	76.83(9)	O6-Gd1-O1	132.23(10)	O7-Tb1-O5	132.34(15)
O5-Sm1-O6	149.07(11)	O4-Eu1-O7	65.35(9)	O6-Gd1-O5	101.67(11)	O7-Tb1-O1	101.21(16)
O5-Sm1-O4	65.07(9)	O4-Eu1-O6	78.06(10)	O2-Gd1-O6	67.03(10)	O4-Tb1-O7	66.86(16)
O5-Sm1-O7	131.94(9)	O4-Eu1-O5	64.47(9)	O2-Gd1-O1	65.29(10)	O4-Tb1-O5	65.55(15)
O5-Sm1-O2	134.64(10)	O4-Eu1-O1	134.42(9)	O2-Gd1-O5	83.44(10)	O4-Tb1-O2	126.44(16)
O1-Sm1-O6	128.90(10)	O9-Eu1-O7	75.66(10)	O1-Gd1-O5	75.69(10)	O4-Tb1-O1	83.44(15)
O1-Sm1-O4	82.13(10)	O9-Eu1-O6	91.69(10)	O4-Gd1-O6	79.08(11)	O5-Tb1-O1	75.88(16)
O1-Sm1-O7	97.44(10)	O9-Eu1-O5	154.71(9)	O4-Gd1-O2	126.03(10)	O2-Tb1-O7	79.28(17)
O1-Sm1-O2	63.94(9)	O9-Eu1-O1	79.56(9)	O4-Gd1-O1	133.59(10)	O2-Tb1-O5	133.49(16)
O1-Sm1-O5	77.36(10)	O9-Eu1-O4	140.76(10)	O4-Gd1-O5	63.25(10)	O2-Tb1-O1	63.33(15)
O9-Sm1-O6	87.00(10)	O2-Eu1-O7	127.43(9)	O9-Gd1-O7	76.85(11)	O9-Tb1-O6	81.13(16)
O9-Sm1-O4	141.88(10)	O2-Eu1-O6	67.03(9)	O9-Gd1-O6	90.22(12)	O9-Tb1-O7	149.44(16)
O9-Sm1-O7	151.21(10)	O2-Eu1-O5	81.81(8)	O9-Gd1-O2	79.35(11)	O9-Tb1-O4	142.34(17)
O9-Sm1-O2	79.04(11)	O2-Eu1-O1	65.34(9)	O9-Gd1-O1	78.64(11)	O9-Tb1-O5	77.21(16)
O9-Sm1-O5	76.86(10)	O2-Eu1-O4	127.24(9)	O9-Gd1-O4	143.22(10)	O9-Tb1-O2	83.42(17)
O9-Sm1-O1	88.09(11)	O2-Eu1-O9	80.21(9)	O9-Gd1-O5	153.32(11)	O9-Tb1-O1	93.13(17)
O11-Sm1-O6	75.91(11)	O11-Eu1-O7	86.62(10)	O11-Gd1-O7	81.52(11)	O9-Tb1-O11	88.58(18)
O11-Sm1-O4	80.02(10)	O11-Eu1-O6	151.14(10)	O11-Gd1-O6	149.33(11)	O11-Tb1-O6	77.46(16)
O11-Sm1-O7	91.31(10)	O11-Eu1-O5	88.49(10)	O11-Gd1-O2	142.12(10)	O11-Tb1-O7	90.73(18)
O11-Sm1-O2	140.87(10)	O11-Eu1-O1	76.50(9)	O11-Gd1-O1	77.28(10)	O11-Tb1-O4	78.66(17)
O11-Sm1-O5	79.50(10)	O11-Eu1-O4	79.23(10)	O11-Gd1-O4	84.09(11)	O11-Tb1-O5	77.81(17)
O11-Sm1-O1	155.16(10)	O11-Eu1-O9	94.75(10)	O11-Gd1-O9	88.10(12)	O11-Tb1-O2	143.90(16)
O11-Sm1-O9	95.38(11)	O11-Eu1-O2	141.81(10)	O11-Gd1-O5	93.21(11)	O11-Tb1-O1	152.55(16)
[1]1-X,2-Y,1-Z		[1]2-X,2-Y,2-Z		[1]2-X,2-Y,2-Z		[1]2-X,1-Y,2-Z	

Table S4 Selected coordination bond angles (°) for **5-8**.

5		**6**		**7**		**8**	
Bond angles containing both dysprosium and copper		Bond angles containing both holmium and copper		Bond angles containing both thulium and copper		Bond angles containing both terbium and copper	
Cu3-O6-Dy1	103.56(19)	Cu3-O6-Ho1	101.50(18)	Cu3-O6-Tm1	100.5(2)	Cu3-O7-Yb1[1]	103.14(16)
Cu1-O6-Dy1	101.37(19)	Cu1-O6-Ho1	101.75(17)	Cu1-O6-Tm1	97.9(2)	Cu1[1]-O7-Yb1[1]	101.41(15)
Cu2-O4-Dy1	99.63(17)	Cu3-O7-Ho1	99.53(15)	Cu3-O7-Tm1[1]	103.2(2)	Cu3-O6-Yb1[1]	100.32(16)
Cu3-O7-Dy1	100.4(2)	Cu2-O7-Ho1	98.20(15)	Cu2-O7-Tm1[1]	102.0(2)	Cu2-O6-Yb1[1]	98.31(16)

Cu2-O7-Dy1	97.74(19)	Cu1-O2-Ho1	101.42(15)	Cu1-O2-Tm1	99.93(18)	Cu2-O4-Yb1[1]	100.19(15)
Cu1-O2-Dy1	101.62(19)			Cu2-O4-Tm1[1]	102.1(2)	Cu1-O2-Yb1	101.96(17)
Bond angles around copper							
O6-Cu3-O6[1]	180.0(3)	O6[1]-Cu3-O6	180.000(1)	O6-Cu3-O61	180.000(1)	O7[1]-Cu3-O7	180.0(2)
O6-Cu3-O7	86.8(2)	O6-Cu3-O7	87.89(16)	O7[1]-Cu3-O6[1]	93.9(2)	O7-Cu3-O6[1]	93.98(16)
O6-Cu3-O71	93.2(2)	O6[1]-Cu3-O7[1]	87.89(16)	O7-Cu3-O6[1]	86.1(2)	O7-Cu3-O6	86.02(16)
O61-Cu3-O7	93.2(2)	O6[1]-Cu3-O7	92.11(16)	O7-Cu3-O6	93.9(2)	O7[1]-Cu3-O6[1]	86.02(16)
O61-Cu3-O7[1]	86.8(2)	O6-Cu3-O7[1]	92.11(16)	O7[1]-Cu3-O6	86.1(2)	O7[1]-Cu3-O6	93.98(16)
O71-Cu3-O7	180.000(1)	O7[1]-Cu3-O7	180.000(1)	O7[1]-Cu3-O7	180.0(3)	O7-Cu3-O10	95.85(15)
O4-Cu2-O7	82.22(18)	O7-Cu2-N2	171.99(17)	O7-Cu2-O4	81.1(2)	O7[1]-Cu3-O10	84.15(15)
O4-Cu2-O10	102.5(2)	O7-Cu2-O10	84.0(2)	O7-Cu2-O10	93.6(2)	O6[1]-Cu3-O6	180.000(1)
O7-Cu2-O10	86.0(3)	O3-Cu2-O7	99.02(15)	O7-Cu2-N2	174.9(2)	O6-Cu3-O10	111.24(17)
O3-Cu2-O4	170.0(2)	O3-Cu2-N2	85.52(16)	O3-Cu2-O7	94.9(2)	O6[1]-Cu3-O10	68.76(17)
O3-Cu2-O7	97.31(19)	O3-Cu2-O4	170.83(16)	O3-Cu2-O4	165.5(2)	O7[1]-Cu1-O8	93.88(16)
O3-Cu2-N1	86.4(2)	O3-Cu2-O10	88.85(18)	O3-Cu2-O10	97.2(2)	O7[1]-Cu1-N1	174.79(19)
O3-Cu2-O10	87.4(2)	N2-Cu2-O10	102.8(2)	O3-Cu2-N2	88.0(2)	O2-Cu1-O7[1]	81.50(16)
O3-Cu2-O4	170.0(2)	O4-Cu2-O7	82.16(15)	O4-Cu2-O10	96.9(2)	O2-Cu1-O8	95.90(18)
O3-Cu2-O7	97.31(19)	O4-Cu2-N2	92.32(16)	O4-Cu2-N2	95.0(2)	O2-Cu1-N1	94.72(19)
O3-Cu2-N1	86.4(2)	O4-Cu2-O10	100.32(18)	N2-Cu2-O10	90.2(2)	O3-Cu1-O7[1]	95.05(16)
O6-Cu1-N2	175.4(2)	O6-Cu1-O2	82.06(16)	O6-Cu1-O8	83.5(2)	O3-Cu1-O2	165.44(17)
O6-Cu1-O8	94.17(18)	O6-Cu1-O8	95.55(17)	O3-Cu1-O6	98.5(2)	O3-Cu1-O8	98.45(17)
O31-Cu1-O6	94.46(18)	O6-Cu1-N1	175.93(19)	O3-Cu1-O2	172.1(2)	O3-Cu1-N1	87.72(19)
O31-Cu1-O2	165.3(2)	O31-Cu1-O6	96.21(16)	O3-Cu1-N1	86.2(2)	N1-Cu1-O8	90.1(2)
O31-Cu1-N2	87.8(2)	O31-Cu1-O2	164.85(16)	O3-Cu1-O8	87.2(2)	O6-Cu2-O4	81.04(16)
O31-Cu1-O8	97.8(2)	O31-Cu1-O8	100.85(16)	O2-Cu1-O6	81.6(2)	O6-Cu2-N2	170.35(19)
O2-Cu1-O6	82.40(18)	O31-Cu1-N1	87.17(17)	O2-Cu1-O8	100.6(2)	O6-Cu2-O10[1]	84.1(2)
O2-Cu1-N2	94.4(2)	O2-Cu1-O8	94.29(16)	N1-Cu1-O6	170.9(2)	O4-Cu2-O10[1]	100.56(18)
O2-Cu1-O8	96.68(19)	O2-Cu1-N1	94.09(17)	N1-Cu1-O2	92.6(2)	O3-Cu2-O6	98.91(16)
N2-Cu1-O8	89.4(2)	N1-Cu1-O8	86.02(18)	N1-Cu1-O8	104.6(3)	O3-Cu2-O4	171.92(17)
						O3-Cu2-N2	85.85(18)
						O3-Cu2-O10[1]	87.45(18)
						N2-Cu2-O4	93.05(18)
						N2-Cu2-O10[1]	104.5(2)
Bond angles around dysprosium		Bond angles around holmium		Bond angles around thulium		Bond angles around ytterbium	
O6-Dy1-O4	128.93(15)	O6-Ho1-O7	70.49(14)	O6-Tm1-O1	134.03(17)	O7[1]-Yb1-O6[1]	69.81(13)
O6-Dy1-O7	68.63(16)	O6-Ho1-O5	147.35(14)	O6-Tm1-O5[1]	101.29(18)	O7[1]-Yb1-O1	132.05(14)
O6-Dy1-O5	146.92(16)	O6-Ho1-O1	131.83(14)	O7[1]-Tm1-O6	69.23(17)	O7[1]-Yb1-O5[1]	145.42(14)
O6-Dy1-O1	130.79(15)	O7-Ho1-O5	133.65(13)	O7[1]-Tm1-O1	146.19(18)	O6[1]-Yb1-O1	101.74(15)
O11-Dy1-O6	77.05(16)	O7-Ho1-O1	99.43(14)	O7[1]-Tm1-O5[1]	131.02(19)	O6[1]-Yb1-O5[1]	133.85(13)
O11-Dy1-O4	79.19(17)	O4-Ho1-O6	130.29(13)	O2-Tm1-O6	68.22(16)	O4[1]-Yb1-O7[1]	129.88(13)
O11-Dy1-O7	90.86(18)	O4-Ho1-O7	67.75(12)	O2-Tm1-O7[1]	130.08(18)	O4[1]-Yb1-O6[1]	67.75(13)
O11-Dy1-O5	77.98(16)	O4-Ho1-O2	127.41(13)	O2-Tm1-O1	65.86(17)	O4[1]-Yb1-O2	125.93(14)

O11-Dy1-O2	143.63(15)	O4-Ho1-O5	65.91(13)	O2-Tm1-O51	82.34(18)	O4[1]-Yb1-O1	82.35(15)
O11-Dy1-O1	151.97(15)	O4-Ho1-O1	81.24(14)	O9-Tm1-O6	92.79(19)	O4[1]-Yb1-O5[1]	66.16(13)
O4-Dy1-O7	67.25(15)	O2-Ho1-O6	66.86(13)	O9-Tm1-O7[1]	77.30(19)	O2-Yb1-O7[1]	67.44(13)
O4-Dy1-O5	65.92(15)	O2-Ho1-O7	78.99(13)	O9-Tm1-O2	79.91(19)	O2-Yb1-O6[1]	78.13(14)
O4-Dy1-O1	83.05(15)	O2-Ho1-O5	130.72(14)	O9-Tm1-O4[1]	143.73(17)	O2-Yb1-O1	64.65(14)
O7-Dy1-O5	133.08(15)	O2-Ho1-O1	64.97(13)	O9-Tm1-O1	77.37(18)	O2-Yb1-O5[1]	133.23(14)
O7-Dy1-O1	102.07(17)	O9-Ho1-O6	83.59(15)	O9-Tm1-O5[1]	151.34(19)	O11-Yb1-O7[1]	76.74(14)
O5-Dy1-O1	75.02(15)	O9-Ho1-O7	152.30(14)	O4[1]-Tm1-O6	77.27(18)	O11-Yb1-O6[1]	92.79(15)
O2-Dy1-O6	66.69(15)	O9-Ho1-O4	139.74(14)	O4[1]-Tm1-O7[1]	66.52(18)	O11-Yb1-O4[1]	79.92(16)
O2-Dy1-O4	126.15(16)	O9-Ho1-O2	82.03(14)	O4[1]-Tm1-O2	125.73(17)	O11-Yb1-O2	144.04(15)
O2-Dy1-O7	78.88(16)	O9-Ho1-O5	73.98(14)	O4[1]-Tm1-O1	133.77(18)	O11-Yb1-O1	150.78(15)
O2-Dy1-O5	133.45(15)	O9-Ho1-O11	90.32(17)	O4[1]-Tm1-O5[1]	64.54(17)	O11-Yb1-O5[1]	77.21(15)
O2-Dy1-O1	64.11(15)	O9-Ho1-O1	90.49(16)	O1-Tm1-O5[1]	74.88(17)	O9-Yb1-O7[1]	81.81(14)
O9-Dy1-O6	81.41(16)	O11-Ho1-O6	77.42(15)	O11-Tm1-O6	149.66(17)	O9-Yb1-O6[1]	150.39(14)
O9-Dy1-O11	88.29(18)	O11-Ho1-O7	93.30(16)	O11-Tm1-O7[1]	81.55(18)	O9-Yb1-O4[1]	141.24(15)
O9-Dy1-O4	142.04(16)	O11-Ho1-O4	79.27(15)	O11-Tm1-O2	141.43(18)	O9-Yb1-O2	83.44(16)
O9-Dy1-O7	149.39(16)	O11-Ho1-O2	144.05(14)	O11-Tm1-O9	88.5(2)	O9-Yb1-O11	88.66(17)
O9-Dy1-O5	76.50(16)	O11-Ho1-O5	79.27(16)	O11-Tm1-O4[1]	83.88(19)	O9-Yb1-O1	90.83(17)
O9-Dy1-O2	83.81(17)	O11-Ho1-O1	150.61(15)	O11-Tm1-O1	75.75(18)	O9-Yb1-O5[1]	75.23(15)
O9-Dy1-O1	92.61(17)	O1-Ho1-O5	72.75(14)	O11-Tm1-O5[1]	91.57(19)	O5[1]-Yb1-O1	74.43(15)
[1]-X,1-Y,1-Z		1-X,2-Y,-Z		[1]-X,2-Y,1-Z		[1]2-X,-Y,1-Z	

Table S5 Geometry analysis using the Shape v 2.0 software.

```
-------------------------------------------------------------------------
S H A P E   v2.0         Continuous Shape Measures calculation
(c) 2010  Electronic Structure Group, Universitat de Barcelona
Contact:  llunell@ub.edu
-------------------------------------------------------------------------

OP-8            1 D8h   Octagon
HPY-8           2 C7v   Heptagonal pyramid
HBPY-8          3 D6h   Hexagonal bipyramid
CU-8            4 Oh    Cube
SAPR-8          5 D4d   Square antiprism
TDD-8           6 D2d   Triangular dodecahedron
JGBF-8          7 D2d   Johnson gyrobifastigium J26
JETBPY-8        8 D3h   Johnson elongated triangular bipyramid J14
JBTPR-8         9 C2v   Biaugmented trigonal prism J50
BTPR-8         10 C2v   Biaugmented trigonal prism
JSD-8          11 D2d   Snub diphenoid J84
TT-8           12 Td    Triakis tetrahedron
```

ETBPY-8 13 D3h Elongated trigonal bipyramid

[ML8]	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
Sm	29.97	24.49	13.75	12.54	4.17	1.72,	11.12	25.86	3.19	2.88	3.15	13.25	23.52
Eu	30.12	24.52	13.85	12.55	4.14	1.64	11.20	25.81	3.12	2.80	3.08	13.27	23.44
Gd	31.22	23.41	15.12	13.07	4.41	1.82	12.57	25.75	2.96	2.38	3.51	13.73	22.91
Tb	31.21	23.61	15.16	13.11	4.30	1.72	12.59	26.09	2.94	2.40	3.43	13.80	23.33
Dy	31.11	23.67	15.31	13.30	4.26	1.68	12.65	25.84	2.79	2.26	3.41	13.98	23.06
Ho	30.87	24.25	14.84	12.66	3.93	1.45	12.35	25.68	2.88	2.48	3.10	13.46	23.16
Tm	31.29	24.16	15.49	13.54	4.17	1.61	12.57	25.76	2.64	2.24	3.29	14.25	23.11
Yb	31.20	24.20	15.56	13.57	4.06	1.56	12.63	25.81	2.58	2.19	3.27	14.30	23.14

Cu1 and Cu2

S H A P E v2.0 Continuous Shape Measures calculation
(c) 2010 Electronic Structure Group, Universitat de Barcelona
Contact: llunell@ub.edu

PP-5 1 D5h Pentagon
vOC-5 2 C4v Vacant octahedron
TBPY-5 3 D3h Trigonal bipyramid
SPY-5 4 C4v Spherical square pyramid
JTBPY-5 5 D3h Johnson trigonal bipyramid J12

[ML5]		PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5
1 (Sm)	Cu1	32.20	1.28	3.86	0.84	6.57
	Cu2	28.92	1.00	5.11	0.78	7.54
2 (Eu)	Cu1	28.74	1.03	5.14	0.79	7.57
	Cu2	32.10	1.28	3.85	0.86	6.52
3 (Gd)	Cu1	25.30	1.66	6.40	1.29	8.87
	Cu2	31.55	1.21	4.36	0.81	7.12
4(Tb)	Cu1	31.29	1.20	4.40	0.85	7.05
	Cu2	25.69	1.59	6.40	1.22	8.80
5(Dy)	Cu1	31.36	1.22	4.32	0.85	7.00
	Cu2	25.39	1.65	6.53	1.30	9.02
6(Ho)	Cu1	29.67	1.38	4.17	1.09	7.03
	Cu2	25.33	1.51	6.30	1.41	8.70
7(Tm)	Cu1	31.29	1.20	4.40	0.85	7.05
	Cu2	31.65	1.30	4.47	0.87	7.32
8(Yb)	Cu1	31.19	1.26	4.43	0.85	7.19

	Cu2	24.92	1.83	6.86	1.52	9.40

Table S6. BVS calculation for O6 and O7 atoms.

atom	BVS calculation	assignment
O6	1.39	OH^-
O7	1.24	OH^-

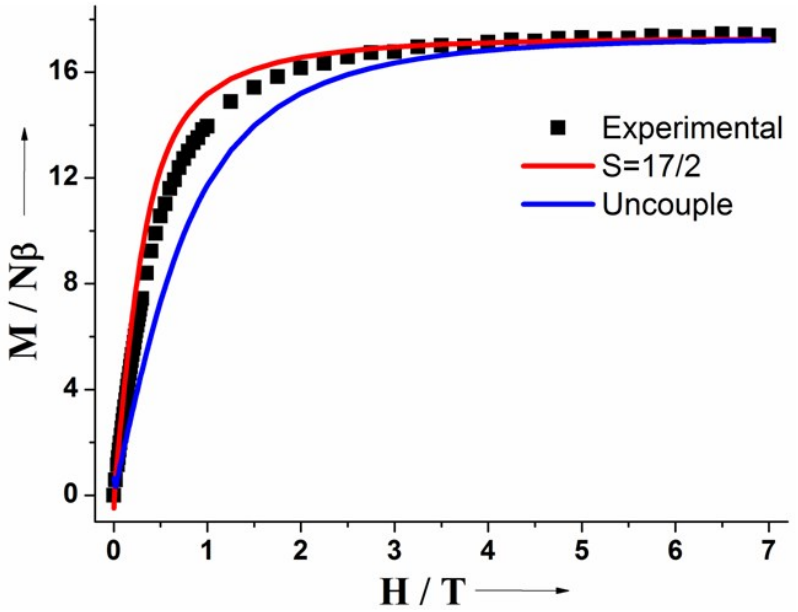

Figure S10 Isothermal field dependent magnetization for **3** at 2 K (black square). The red solid line represents the Brillouin function for five uncoupled Cu and two isolated Gd centers (g_{Gd} = g_{Cu} = 2.03), and blue solid line represents an S = 17/2 state (g_{Gd} = g_{Cu} = 2.03), respectively.

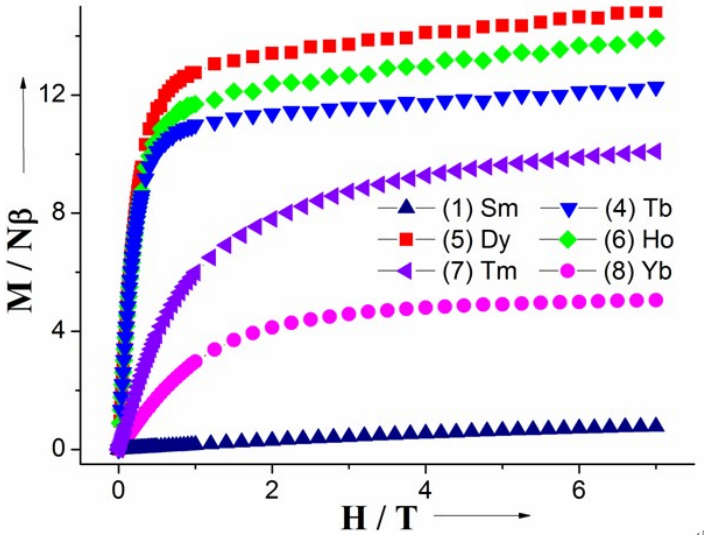

Figure S11 Field dependence of the magnetization for complexes **1** and **4-8** in the field range of 0.0-7.0 T at 2.0 K.

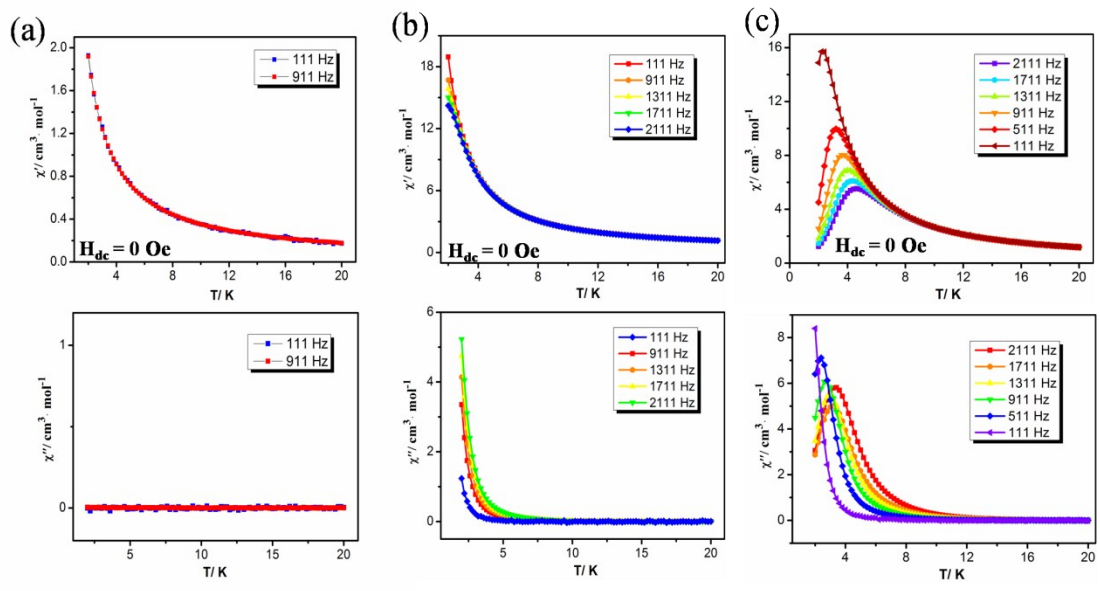

Figure S12 Temperature dependence of the in-phase (χ′) and out-of-phase (χ″) ac susceptibilities in the range of 111-2111 Hz at H_{ac} = 3.0 Oe for (a) Cu^{II}-Dy^{III}, (b) Cu^{II}-Ho^{III} and (c) Cu^{II}-Tb^{III} measured without applied dc field.

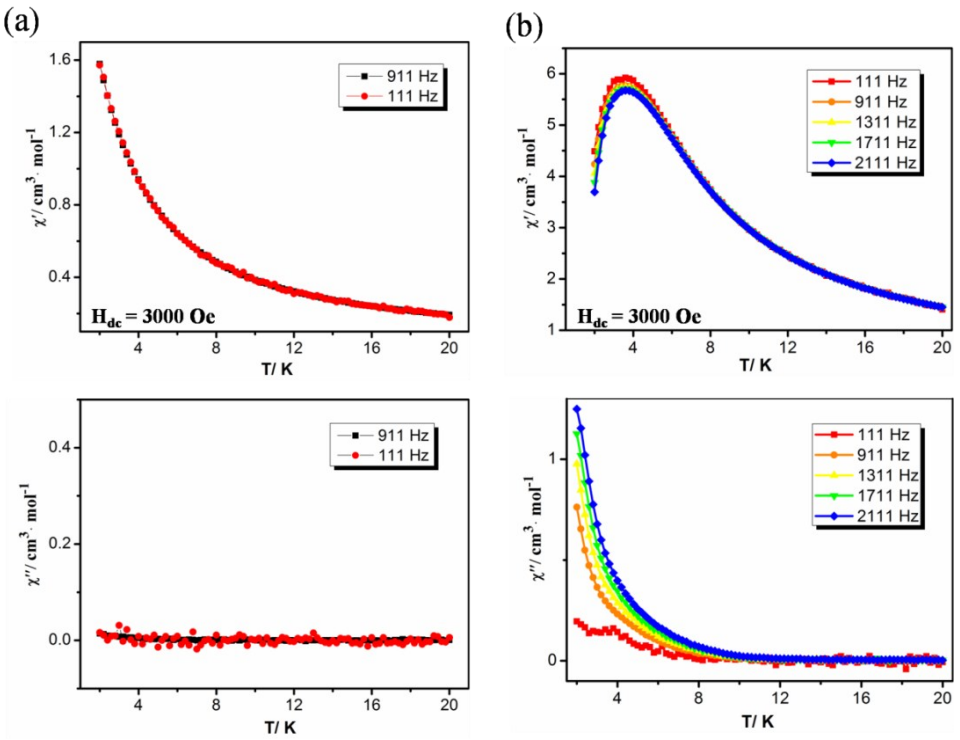

Figure S13 Temperature dependence of the in-phase (χ′) and out-of-phase (χ″) ac susceptibilities in the range of 111-2111 Hz at Hac = 3.0 Oe for (a) Cu^{II}-Dy^{III} and (b) Cu^{II}-Ho^{III} measured with a 3000 Oe dc field.

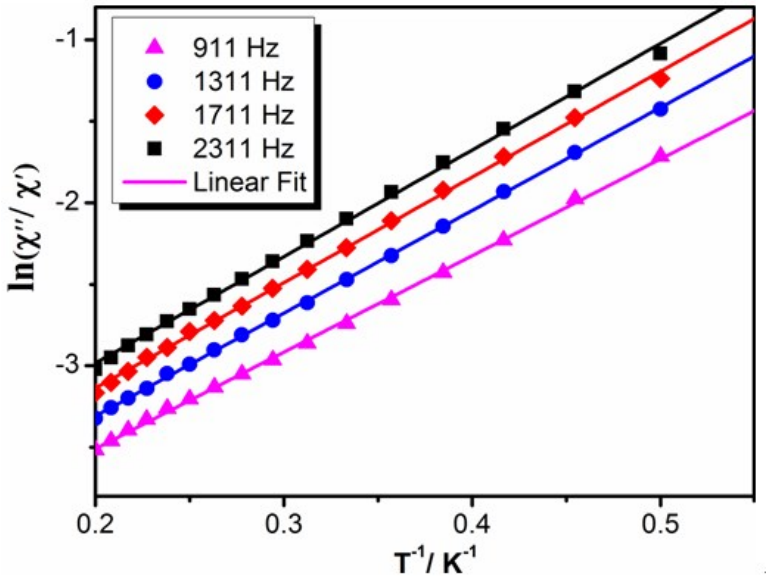

Figure S14 Plots of $\ln\left(\chi''/\chi'\right)$ vs. 1/T for Cu^{II}-Ho^{III} complex. The solid lines represent the fitting results over the temperature range of 2.0–6.0 K.

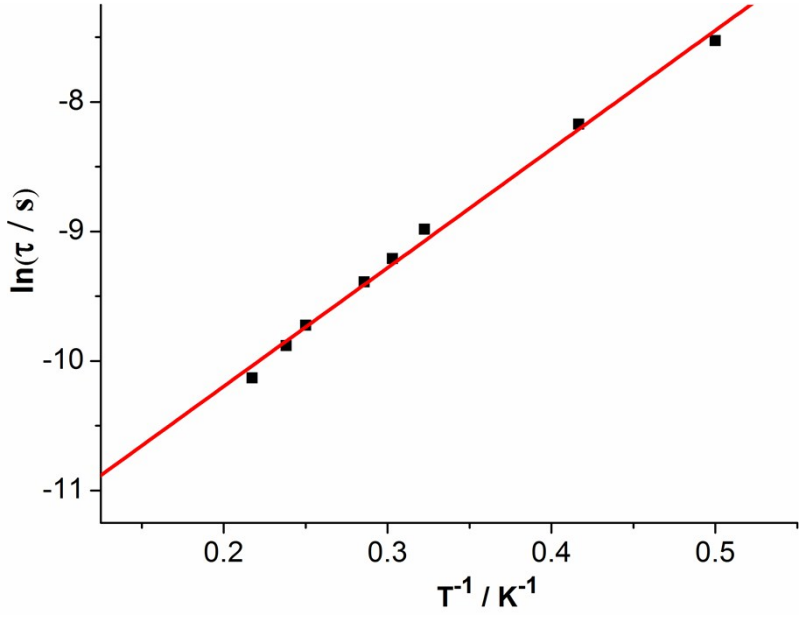

Figure S15 Plots of ln τ vs. T^{-1} of Cu^{II}-Tb^{III} complex frequency dependence measurement under 3000 Oe and 2.0 K- 4.6 K.