Supporting Information

for manuscript:

Two-dimensional 3d-4f Heterometallic Coordination Polymers: Syntheses, Crystal Structures, and Magnetic Properties of Six New Co(II)–Ln(III) Compounds

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Table S1. Selected intermolecular contacts in **1-2**

	Intermolecular O···O distances (Å)				
	1	**2**		**1**	**2**
O(1)···O(1w)	2.943(7)	2.922(6)	O(3w)···O(4w)$^{(d-1)}$	3.059(9)	3.088(9)
O(1)···O(6w)$^{(f-1)}$	2.743(8)	3.109(6)	O(4) ···O(7w)$^{(o-1)}$	2.802(9)	2.812(12)
O(1w)···O(2w)	2.808(6)	2.744(6)	O(4) ···O(6w)	2.997(8)	2.963(8)
O(1w)···O(3)$^{(f-1)}$	2.786(7)	2.762(6)	O(4w)$^{(e-1)}$···O(6)	2.816(9)	2.830(9)
O(1w)···O(7)$^{(c-1)}$	2.848(7)	2.811(7)	O(4w)···O(5w)	2.876(9)	2.902(9)
O(1w)···O(7)$^{(a-1)}$	3.021(7)	2.964(7)	O(4w)···O(5w)$^{(d-1)}$	3.011(9)	2.995(9)
O(2)···O(2w)	2.877(6)	2.847(6)	O(4w)···O(8w)	2.781(10)	2.743(10)
O(2)···O(2w)$^{(b-1)}$	3.024(7)	2.952(7)	O(5w)···O(10w)	2.705(16)	2.698(15)
O(2w)···O(8w)$^{(a-1)}$	2.909(8)	2.921(8)	O(5w)···O(6w)$^{(p-1)}$	2.820(9)	2.816(9)
O(2w)···O(10w)$^{(h-1)}$	2.808(14)	2.843(14)	O(6) ···O(7w)$^{(g-1)}$	2.656(10)	2.610(13)
O(2w)···O(5)$^{(i-1)}$	2.711(6)	2.720(6)	O(6) ···O(9w)$^{(g-1)}$	2.980(11)	2.936(10)
O(3w)···O(5w)	3.043(8)	3.019(8)	O(6w)···O(8w)$^{(s-1)}$	2.806(10)	2.818(10)
O(3w)···O(5w)$^{(d-1)}$	2.918(10)	2.901(11)	O(7w)···O(10w)$^{(l-1)}$	3.03(2)	3.098(17)
O(3w)···O(9w)$^{(n-1)}$	2.801(11)	2.779(10)	O(7w)···O(10w)$^{(i-1)}$	2.83(2)	2.686(18)
O(3w)···O(4)$^{(j-1)}$	2.763(9)	2.780(10)	O(8) ···O(8w)$^{(e-1)}$	3.070(8)	3.040(8)
O(3w)···O(4w)	2.876(9)	2.874(9)	O(9w)···O(8w)$^{(r-1)}$	2.899(12)	2.925(11)

Symmetry code: (*a-1*) = 1/2-*x*,1/2+*y*,3/2-z; (*b-1*) =1-*x*,2-*y*,2-z; (*c-1*) =1/2+*x*,5/2-*y*,1/2+*z*; (*d-1*)= -*x*,2-*y*,-*z*; (*e-1*) = -x,2-y,1-z (*f-1*)=*x*,1+*y*, *z*; (*g*-1) = -1+*x*, *y*, *z*; (*h-1*)= *x*, *y*, *1+z*; (*i-1*)=1/2+*x*,3/2-*y*,1/2+*z*; (*j-1*)= *x*, *y*, -1+*z*; (*k-1*)=1-*x*,1-*y*,1-*z;* (*l-1*)=1-*x*,2-*y*,1-*z*; (*m*-1)=-x,1-y,1-z; (*n*-1) = -1+x, y, -1+z; (*o*-1)= -1/2+x, 3/2-y, 1/2+z; (*p*-1) = *x*, 1+*y*, -1+*z*.

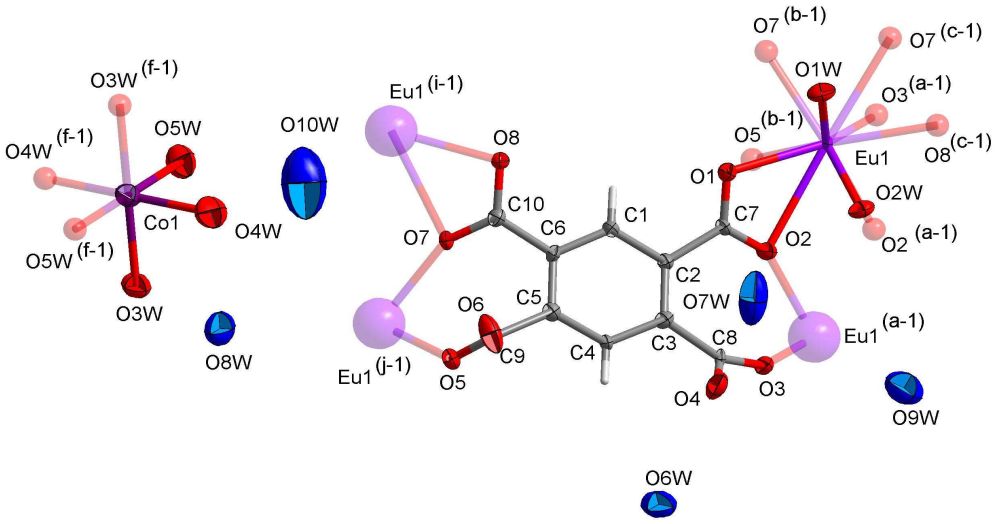

Figure S1. A perspective view of a asymmetric unit of **2** showing the atom numbering and the coordination mode of the bta ligand.

Table S2. Selected Bond Lengths (Å), and Angles (deg) in **1-2**

	1	**2**		**1**	**2**
Ln(1)-O(1)	2.537(5)	2.476(4)	Ln(1)-O(3)$^{(b-1)}$	2.502(5)	2.475(5)
Ln(1)-O(1w)	2.545(5)	2.495(5)	Ln(1)-O(7)$^{(c-1)}$	2.695(4)	2.702(4)
Ln(1)-O(2)	2.713(4)	2.709(4)	Ln(1)-O(8)$^{(c-1)}$	2.513(5)	2.465(4)
Ln(1)-O(2w)	2.543(5)	2.485(5)	Co(1)-O(5w)	2.090(6)	2.069(5)
Ln(1)-O(5)$^{(a-1)}$	2.477(5)	2.425(5)	Co(1)-O(3w)	2.125(6)	2.118(5)
Ln(1)-O(7)$^{(a-1)}$	2.476(4)	2.430(4)	Co(1)-O(4w)	2.073(6)	2.100(6)
Ln(1)-O(2)$^{(b-1)}$	2.436(4)	2.393(4)			
O(1)-Ln(1)-O(1w)	70.8(2)	72.0(2)	O(2)-Ln(1)-O(2)$^{(b-1)}$	62.4(2)	61.7(2)
O(1)-Ln(1)-O(2)$^{(b-1)}$	111.43(14)	110.81(15)	O(2)-Ln(1)-O(2w)	66.3(2)	66.32(15)
O(1)-Ln(1)-O(2w)	77.8(2)	77.6(2)	O(2)-Ln(1)-O(3)$^{(b-1)}$	118.11(15)	117.77(15)
O(1)-Ln(1)-O(3)$^{(b-1)}$	145.5(2)	144.8(2)	O(2)-Ln(1)-O(5)$^{(a-1)}$	65.6(2)	65.67(15)
O(1)-Ln(1)-O(5)$^{(a-1)}$	73.4 (2)	73.4(2)	O(2)-Ln(1)-O(7)$^{(a-1)}$	119.09(15)	119.17(15)
O(1)-Ln(1)-O(7)$^{(a-1)}$	79.4(2)	79.37(15)	O(2)-Ln(1)-O(8)$^{(c-1)}$	126.50(15)	126.52(14)
O(1)-Ln(1)-O(8)$^{(c-1)}$	142.6(2)	143.1(2)	O(2w)-Ln(1)-O(3)$^{(b-1)}$	130.7(2)	131.59(15)
O(1w)-Ln(1)-O(2)	108.7(2)	109.78(15)	O(2w)-Ln(1)-O(5)$^{(a-1)}$	131.8(2)	131.9(2)
O(1w)-Ln(1)-O(2w)	67.0(2)	66.9(2)	O(2w)-Ln(1)-O(7)$^{(a-1)}$	139.4(2)	139.0(2)
O(1w)-Ln(1)-O(3)$^{(b-1)}$	133.2(2)	132.4(2)	O(2w)-Ln(1)-O(8)$^{(c-1)}$	69.8(2)	70.3(3)
O(1w)-Ln(1)-O(5)$^{(a-1)}$	133.4(2)	134.17(15)	O(3w)-Co(1)-O(4w)	86.4(3)	85.9(3)
O(1w)-Ln(1)-O(7)$^{(a-1)}$	74.0(2)	74.0(2)	O(3w)-Co(1)-O(5w)	92.4(3)	92.3(3)
O(1w)-Ln(1)-O(8)$^{(c-1)}$	79.5(2)	78.8(2)	O(4w)-Co(1)-O(5w)	87.4(3)	88.2(3)

Symmetry code: (*a-1*) =1-*x*, 2-*y*, 2-*z*; (*b-1*) =0.5-*x*,0.5-*y*,1.5-*z*; (*c-1*) =0.5+*x*,2.5-*y*,1/2+*z*.

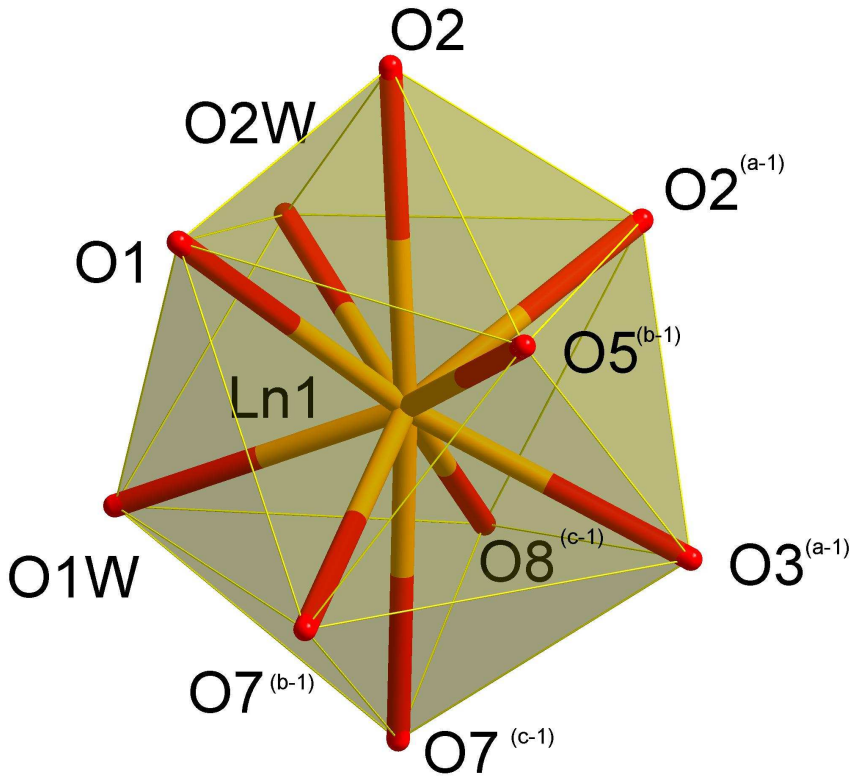

Figure S2. A perspective view of the ten coordinated lanthanide environments together with the atom numbering scheme for compound **1-2** following the main text symmetry code.

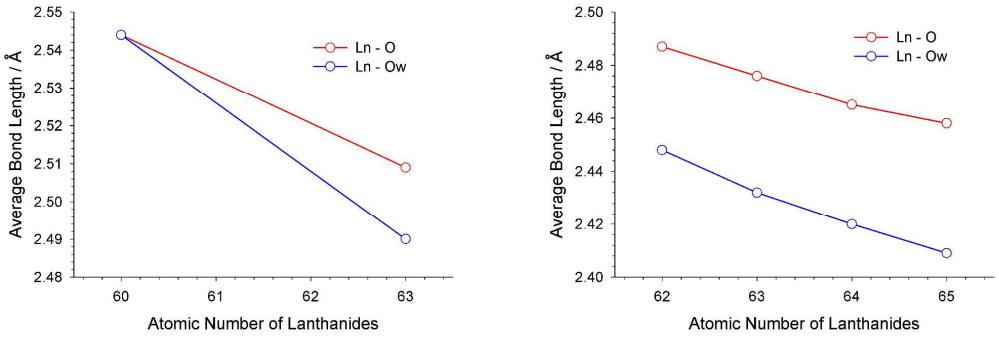

Figure S3. Variation of the average values of the Ln-Ocarboxylate and Ln-Owater bond lengths with the atomic number for the **1-2** (left) and **3-6** (right) compounds.

Table S3. Selected intermolecular contacts for **3-6** compounds

Intermolecular O···O distances (Å)				
	3	**4**	**5**	**6**
O(1w)···O(3)	2.751(6)	2.771(5)	2.741(5)	2.735(8)
O(1w)···O(6w)$^{(f-2)}$	2.846(8)	2.853(8)	2.839(8)	2.845(12)
O(1w)···O(3w)	2.908(4)	2.920(4)	2.894(5)	2.877(6)
O(1w)···O(8)$^{(g-2)}$	2.905(6)	2.898(5)	2.915(5)	2.919(8)
O(1w)···O(2w)	2.949(4)	2.960(4)	2.934(4)	2.921(7)
O(1w)···O(8)$^{(c-2)}$	2.963(5)	2.992(4)	2.954(5)	2.919(8)
O(2w)···O(7w)	2.637(10)	2.629 (10)	2.641(9)	2.64(2)
O(2w)···O(5w)$^{(g-2)}$	2.832(6)	2.816(6)	2.829 (6)	2.817(9)
O(2w)···O(2)$^{(a-2)}$	2.975(5)	2.993(4)	2.947(4)	2.959(7)
O(2w)···O(3)	3.005(5)	3.022(4)	2.990(4)	2.970(8)
O(2w)···O(7)$^{(b-2)}$	3.100(6)	3.123(6)	3.086(6)	3.075(9)
O(2w)···O(3w)	3.118(5)	3.143(4)	3.093(5)	3.072(7)
O(3w)···O(2)$^{(g-2)}$	2.706(4)	2.705(3)	2.705(4)	2.707(7)
O(3w)···O(5w)$^{(a-2)}$	2.803(6)	2.809(5)	2.797(6)	2.816(8)
O(3w)···O(8)$^{(c-2)}$	2.836(5)	2.851(4)	2.823(4)	2.809(7)
O(3w)···O(2)$^{(a-2)}$	2.848(5)	2.859(4)	2.835(4)	2.826(7)
O(3w)···O(1)$^{(a-2)}$	3.192(5)	3.219(4)	3.175(5)	3.147(8)
O(4w)···O(5)$^{(e-2)}$	2.642(4)	2.642(3)	2.644(4)	2.653(6)
O(4w)···O(3)$^{(d-2)}$	2.765(4)	2.765(3)	2.769(4)	2.769(6)
O(4w)···O(4)	2.886(5)	2.889(10)	2.890(5)	2.908(8)
O(4w)···O(6)$^{(b-2)}$	2.970(5)	2.970(4)	2.964(5)	2.964(7)
O(4w)···O(6)$^{(e-2)}$	2.976(5)	2.983(4)	2.982(5)	2.989(7)
O(4w)···O(7w)$^{(d-2)}$	3.010(13)	3.018(12)	2.997(12)	2.98(2)
O(4w)···O(6w)	3.093(8)	3.098(7)	3.086(7)	3.082(11)
O(4w)···O(4)$^{(d-2)}$	3.098(5)	3.104(4)	3.093(5)	3.096(8)
O(5w)···O(5)$^{(f-2)}$	2.822(8)	2.842(8)	2.833(8)	2.813(12)
O(5w)···O(4)	2.982(9)	2.982(8)	2.978(9)	2.965(13)
O(6w)···O(7w)$^{(h-2)}$	2.685(11)	2.667(10)	2.691(11)	2.66(2)
O(6w)···O(6)$^{(b-2)}$	2.891(12)	2.865(11)	2.887(12)	2.89(2)
O(7w)···O(5)$^{(i-2)}$	2.895(9)	2.902(9)	2.898(8)	2.909(13)

Symmetry code: (*a-2*) = 1-*x*, 1-*y*, 2-*z*; (*b-2*) =1+*x*, -1+*y*, *z*; (*c-2*) =-*x*, 2-*y*, 2-*z*; (*d-2*) = 1-*x*, 1-*y*, 1-*z*; (*e-2*) = -*x*, 2-*y*, 1-*z*; (*f-2*) = *x*, 1+*y*, *z*; (*g-2*) =1+*x*, *y*, *z*; (*h-2*) = *x*, -1+*y*, *z*; (*i-2*) =1-*x*, 2-*y*, 1-*z*

Table S4. Selected Bond Lengths (Å), and Angles (deg) for **3-6** compounds

	3	**4**	**5**	**6**
Ln(1)-O(1)	2.453(3)	2.467(2)	2.444(3)	2.433(4)
Ln(1)-O(1)$^{(a-2)}$	2.490(2)	2.506(2)	2.475(3)	2.465(4)
Ln(1)-O(1w)	2.440(3)	2.458(2)	2.432(3)	2.4168(2)
Ln(1)-O(2)$^{(a-2)}$	2.671(3)	2.674(2)	2.663(2)	2.671(4)
Ln(1)-O(2w)	2.417(4)	2.431(2)	2.402(4)	2.401(5)
Ln(1)-O(3)	2.414(2)	2.428(2)	2.404(2)	2.396(4)
Ln(1)-O(3w)	2.440(4)	2.455(3)	2.427(4)	2.409(5)
Ln(1)-O(7)$^{(b-2)}$	2.385(3)	2.395(2)	2.374(3)	2.363(4)
Ln(1)-O(8)$^{(c-2)}$	2.443(3)	2.454(3)	2.432(2)	2.423(4)
Co(1)-O(4)	2.120(3)	2.120(3)	2.115(2)	2.123(4)
Co(1)-O(4)$^{(d-2)}$	2.120(3)	2.120(3)	2.115(2)	2.123(4)
Co(1)-O(4w)	2.114(4)	2.119(3)	2.118(4)	2.125 (5)
Co(1)-O(4w)$^{(d-2)}$	2.114(4)	2.119(3)	2.118(4)	2.125 (5)
Co(1)-O(6) $^{(e-2)}$	2.091(3)	2.089(2)	2.087(2)	2.084(4)
Co(1)-O(6) $^{(b-2)}$	2.091(3)	2.089(2)	2.087(2)	2.084(4)
O(4)-Co(1)-O(4w)$^{(d-2)}$	94.05(13)	94.12(11)	93.85(13)	93.6(2)
O(4)-Co(1)-O(4w)	85.95(13)	85.88(11)	86.13(14)	86.4(2)
O(4)-Co(1)-O(6)$^{(b-2)}$	95.03(13)	94.99(10)	94.89(11)	95.0(2)
O(4)-Co(1)-O(6)$^{(e-2)}$	84.97(13)	85.01(10)	85.11(11)	85.1(2)
O(4w)-Co(1)-O(6))$^{(b-2)}$	89.87(13)	89.76(10)	89.66(12)	89.5 (2)
O(4w)- Co(1)-O(6) $^{(e-2)}$	90.13(13)	90.24(10)	90.34(12)	90.5(2)
O(2w)-Ln(1)-O(3)	76.93(11)	76.920(2)	76.94(10)	77.0(2)
O(2w)-Ln(1)-O(3w)	79.86(13)	80.049(2)	79.65(13)	79.4(2)
O(2w)-Ln(1)-O(1w)	74.78(13)	74.537(2)	74.72(13)	74.6(2)
O(2w)-Ln(1)-O(8)$^{(c-2)}$	142.63(13)	142.841(2)	142.53(11)	141.9(2)
O(2w)-Ln(1)-O(1)	141.92(13)	141.780(3)	142.23(11)	142.4(2)
O(2w)-Ln(1)-O(1)$^{(a-2)}$	121.28(11)	121.495(2)	121.09(10)	121.4(2)
O(2w)-Ln(1)-O(2)$^{(a-2)}$	71.37(13)	71.612(2)	70.95(11)	71.2(2)
O(2w)-Ln(1)-O(7)$^{(b-2)}$	80.43(11)	80.623(3)	80.48(11)	80.4(2)
O(3) -Ln(1)-O(3w)	139.57(11)	139.505(2)	139.47(10)	139.4(2)
O(3) -Ln(1)-O(1w)	69.05(11)	69.075(2)	69.05(10)	69.2(2)
O(3) -Ln(1)-O(8)$^{(c-2)}$	111.10(10)	110.987(1)	111.24(8)	111.54(14)
O(3) -Ln(1)-O(1)	72.42(10)	72.322(2)	72.71(8)	73.0(2)
O(3) -Ln(1)-O(1)$^{(a-2)}$	139.74(8)	139.629(2)	139.81(8)	140.13(12)
O(3) -Ln(1)-O(2)$^{(a-2)}$	132.25(10)	132.551(2)	131.97(8)	131.50(14)
O(3)-Ln(1)-O(7)$^{(b-2)}$	74.60(9)	74.648(2)	74.50(8)	74.3(3)
O(3w)-Ln(1)-O(1w)	73.15(12)	72.923(2)	73.11(12)	73.2(2)
O(3w)-Ln(1)-O(8)$^{(c-2)}$	71.03(12)	71.002(2)	71.04(10)	71.1(2)
O(3w)-Ln(1)-O(1)	138.12(11)	138.078(3)	138.00(11)	138.1(2)
O(3w)-Ln(1)-O(1)$^{(a-2)}$	80.70(10)	113.519(3)	80.72(10)	80.4(2)
O(3w)-Ln(1)-O(2)$^{(a-2)}$	67.56(12)	67.614(2)	67.51(10)	67.4(2)
O(3w)-Ln(1)-O(7)$^{(b-2)}$	133.97(10)	133.285(2)	133.01(10)	132.6(2)
O(1w)-Ln(1)-O(8)$^{(c-2)}$	74.72(11)	75.027(2)	74.77(10)	74.2(2)
O(1w)-Ln(1)-O(1)	113.28(12)	113.519(3)	113.40(11)	113.2(2)
O(1w)-Ln(1)-O(1)$^{(a-2)}$	146.39(10)	146.451(2)	146.47(10)	146.0(2)
O(1w)-Ln(1)-O(2)$^{(a-2)}$	131.49(10)	131.299(3)	131.20(10)	131.3(2)
O(1w)-Ln(1)-O(7)$^{(b-2)}$	139.58(9)	139.614(4)	139.48(10)	140.0(2)
O(1)-Ln(1)-O(1)$^{(a-2)}$	73.61(8)	73.481(2)	73.53(8)	73.64(14)
O(1)-Ln(1)-O(2)$^{(a-2)}$	114.87(10)	114.810(3)	115.05(9)	115.1(2)
O(1) -Ln(1)-O(7)$^{(b-2)}$	70.14(10)	69.863(3)	70.21(9)	70.7(2)
O(1) -Ln(1)-O(8)$^{(c-2)}$	71.34(11)	71.2(1)	71.2(1)	71.4(2)
O(1) $^{(a-20)}$-Ln(1)-O(7)$^{(b-2)}$	74.0(1)	73.927(2)	74.03(8)	74.54 (13)
O(1) $^{(a-20)}$-Ln(1)-O(8)$^{(c-2)}$	77.1(1)	76.9 (1)	77.2(1)	77.24(14)
O(1) $^{(a-20)}$-Ln(1)-O(2)$^{(a-2)}$	50.0(1)	49.98(8)	50.2(1)	50.34(14)
O(7)$^{(b-20)}$-Ln(1)- O(2)$^{(a-2)}$	66.0(1)	66.01(8)	65.9(1)	65.57(14)
O(7)$^{(b-20)}$-Ln(1)- O(8)$^{(c-2)}$	136.82(10)	136.423(2)	136.85(8)	137.61 (14)

Symmetry code: (*a-2*) = 1-*x*, 1-*y*, 2-*z*; (*b-2*) =1+*x*, -1+*y*, *z*; (*c-2*) =-*x*, 2-*y*, 2-*z*; (*d-2*) = 1-*x*, 1-*y*, 1-*z*; (*e-2*) = -*x*, 2-*y*, 1-*z*.

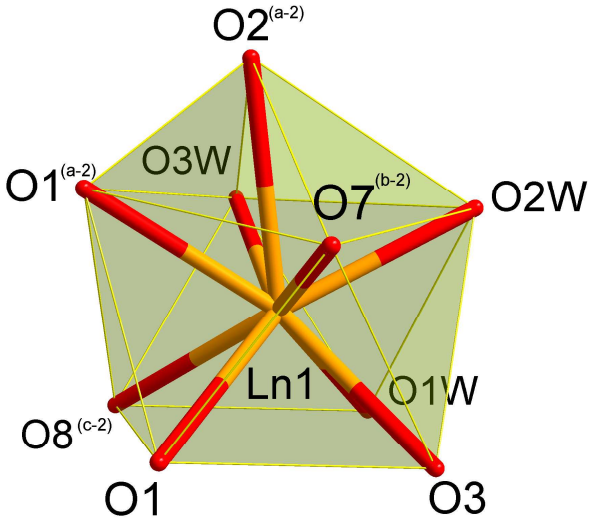

Figure S4. A perspective view of the lanthanide environments of **3-6** together with the atom numbering scheme.

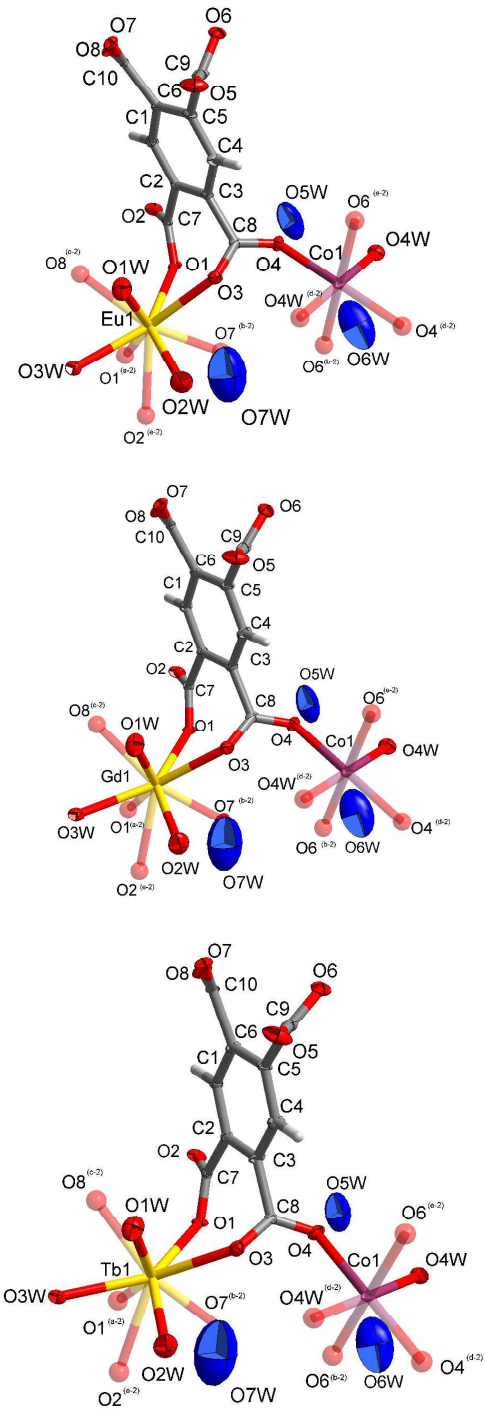

Figure S5. A perspective view of the crystallographically independent units with the numbering scheme of complexes **3**, **5** and **6**.

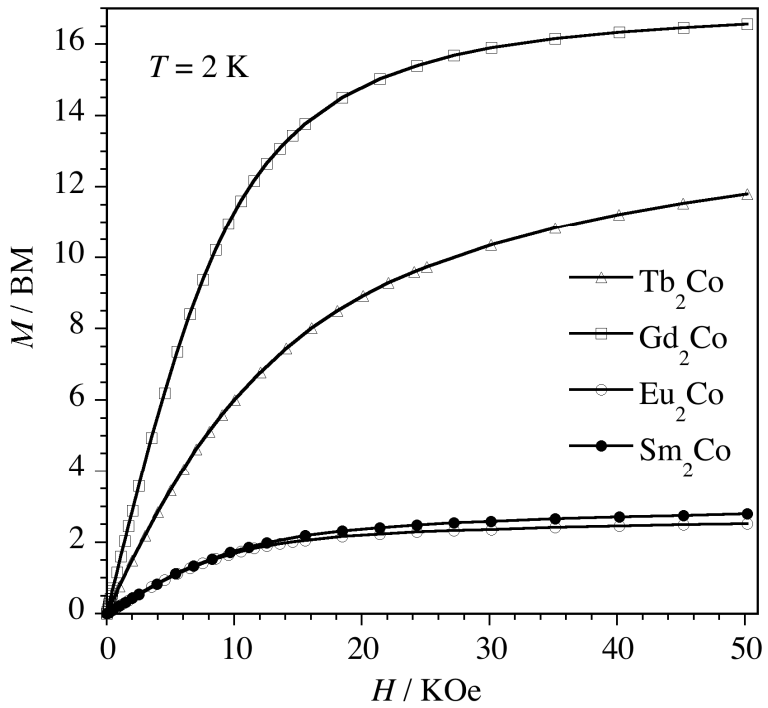

Figure S6. Magnetization *vs* H plot at 2.0 K for $Ln^{III}_2Co^{II}$ [Ln = Eu (**3**), Sm (**4**), Gd (**5**) and Tb (**6**)]. The solid lines are only eye-guides.

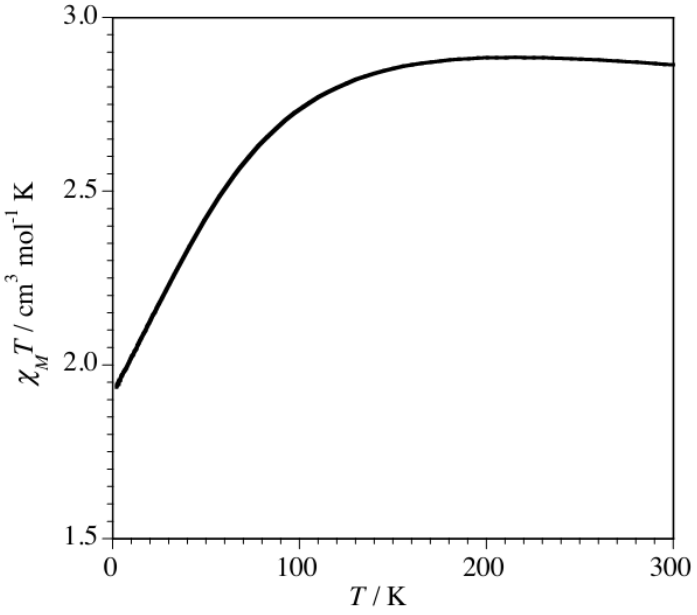

Figure S7. Theoretical curve for the Co(II) ion, calculated from the best-fit parameters according to equation 5-10, for compound **5** (see manuscript text).