Electronic Supplementary Information (ESI)

Three 3d-4f Heterometallic Complexes Constructed from Oxalic Acid and Benzimidazole-5,6-dicarboxylic Acid

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Table S1 Selected Bond Lengths (Å) and Angles (°) for 1-3.

	1	2	3
Co(1)-N(1)	2.117(3)	2.112(2)	2.115(4)
Co(1)-O(1)	2.124(3)	2.125(2)	2.120(3)
Co(1)-O(2)	2.101(2)	2.104(2)	2.097(3)
Co(2)-N(3)	2.144(3)	2.147(3)	2.148(4)
Co(2)-O(3)	2.100(2)	2.097(2)	2.096(3)
Co(2)-O(4)	2.106(3)	2.106(2)	2.105(3)
Co(2)-O(5)	2.018(2)	2.017(2)	2.008(3)
Co(2)-O(9)	2.080(2)	2.079(2)	2.078(3)
Co(2)-O(13)	2.186(3)	2.187(2)	2.184(4)
Ln(1)-O(6)	2.347(2)	2.338(2)	2.306(3)
Ln(1)-O(7)#1	2.366(2)	2.355(2)	2.346(3)
Ln(1)-O(8)#10	2.398(2)	2.381(2)	2.321(3)
Ln(1)-O(10)	2.619(2)	2.603(2)	2.578(3)
Ln(1)-O(10)#1	2.530(2)	2.519(2)	2.516(3)
Ln(1)-O(11)	2.444(2)	2.430(2)	2.400(3)
Ln(1)-O(11)#8	2.653(2)	2.641(2)	2.628(3)
Ln(1)-O(12)#8	2.444(2)	2.428(2)	2.397(3)
O(2)#2-Co(1)-O(2)	180.000(2)	180.000(1)	180.00(17)
O(2)-Co(1)-N(1)#3	84.31(10)	84.44(9)	84.72(14)
O(2)-Co(1)-N(1)#4	95.69(10)	95.56(9)	95.28(14)
N(1)#3-Co(1)-N(1)#4	180.000(1)	180.000(1)	180.0(2)
O(2)-Co(1)-O(1)#2	100.23(10)	100.23(9)	100.23(13)
N(1)#3-Co(1)-O(1)#2	94.00(11)	94.46(9)	94.68(14)
N(1)#4-Co(1)-O(1)#2	86.00(11)	85.54(9)	85.32(14)
O(2)-Co(1)-O(1)	79.77(10)	79.77(9)	79.77(13)
O(1)#2-Co(1)-O(1)	180.000(1)	180.000(1)	180.00(8)
O(5)-Co(2)-O(9)	108.69(10)	108.25(9)	107.54(13)
O(5)-Co(2)-O(3)	162.33(10)	162.46(9)	162.88(13)
O(9)-Co(2)-O(3)	88.37(10)	88.71(9)	89.02(13)
O(5)-Co(2)-O(4)	83.74(10)	83.89(9)	84.29(13)
O(9)-Co(2)-O(4)	165.92(10)	166.21(9)	166.69(15)
O(3)-Co(2)-O(4)	78.80(10)	78.77(9)	78.80(13)
O(5)-Co(2)-N(3)#5	90.75(10)	91.00(9)	91.14(14)
O(9)-Co(2)-N(3)#5	91.31(11)	91.18(10)	90.79(14)
O(3)-Co(2)-N(3)#5	93.51(11)	93.15(9)	92.99(14)
O(4)-Co(2)-N(3)#5	95.22(11)	95.22(10)	95.16(15)
O(5)-Co(2)-O(13)	89.98(10)	89.81(9)	90.04(14)
O(9)-Co(2)-O(13)	85.89(10)	85.95(9)	85.81(14)
O(3)-Co(2)-O(13)	86.60(10)	86.88(9)	86.79(14)
O(4)-Co(2)-O(13)	87.55(11)	87.62(10)	88.13(14)
N(3)#5-Co(2)-O(13)	177.20(11)	177.12(10)	176.60(14)
O(6)-Ln(1)-O(7)#1	139.64(8)	139.72(7)	140.51(11)
O(6)-Ln(1)-O(8)#10	69.27(8)	69.36(8)	69.63(11)
O(7)#1-Ln(1)-O(8)#10	149.31(8)	149.19(8)	148.23(11)
O(6)-Ln(1)-O(12)#8	84.48(9)	84.48(8)	84.23(11)
O(7)#1-Ln(1)-O(12)#8	94.19(9)	94.42(8)	94.85(12)

O(8)#10-Ln(1)-O(12)#8	100.11(9)	99.65(8)	99.20(12)
O(6)-Ln(1)-O(11)	116.11(8)	116.12(7)	116.36(11)
O(7)#1-Ln(1)-O(11)	76.48(8)	76.47(8)	76.20(11)
O(8)#10-Ln(1)-O(11)	80.05(9)	80.08(8)	79.82(11)
O(12)#8-Ln(1)-O(11)	157.29(8)	157.11(7)	156.81(11)
O(6)-Ln(1)-O(10)#1	136.57(8)	136.83(7)	136.91(10)
O(7)#1-Ln(1)-O(10)#1	82.56(8)	82.28(7)	81.36(11)
O(8)#10-Ln(1)-O(10)#1	72.84(8)	72.79(7)	72.72(11)
O(12)#8-Ln(1)-O(10)#1	81.97(8)	82.09(7)	81.80(10)
O(11)-Ln(1)-O(10)#1	76.36(7)	75.94(6)	75.77(10)
O(6)-Ln(1)-O(10)	74.17(8)	73.88(7)	73.79(10)
O(7)#1-Ln(1)-O(10)	72.58(8)	72.78(7)	73.52(11)
O(8)#10-Ln(1)-O(10)	119.98(8)	120.26(7)	120.44(11)
O(12)#8-Ln(1)-O(10)	121.98(7)	121.90(6)	122.07(10)
O(11)-Ln(1)-O(10)	75.44(7)	75.94(6)	76.42(10)
O(10)#1-Ln(1)-O(10)	145.93(4)	145.95(4)	146.12(6)
O(6)-Ln(1)-O(11)#8	74.48(8)	74.52(7)	74.84(11)
O(7)#1-Ln(1)-O(11)#8	73.71(8)	73.75(7)	74.00(10)
O(8)#10-Ln(1)-O(11)#8	135.61(8)	135.61(7)	136.10(10)
O(12)#8-Ln(1)-O(11)#8	50.92(7)	51.22(6)	51.59(10)
O(11)-Ln(1)-O(11)#8	140.53(5)	140.60(4)	140.65(7)
O(10)#1-Ln(1)-O(11)#8	123.78(7)	123.93(6)	123.50(10)
O(10)-Ln(1)-O(11)#8	71.36(7)	71.02(6)	70.91(9)

Symmetry transformations used to generate equivalent atoms: For **1** and **2** #1 -x+1, y-1/2, -z+3/2; #2 -x, -y+1, -z+2; #3 x-1, y, z; #4 -x+1, -y+1, -z+2; #5 -x, y+1/2, -z+3/2; #8 -x+1, y+1/2, -z+3/2; #10 x, y-1, z; For **3** #1 x, y+1, z; #2 -x+2, -y+1, -z; #3 -x+1, -y+1, -z; #4 x+1, y, z; #5 -x+2, y-1/2, -z+1/2; #8 -x+1, y-1/2, -z+1/2; #10 -x+1, y+1/2, -z+1/2.

Table S2. Hydrogen bond lengths (Å) and bond angles (°) for complexes **1-3**

	D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
1	N(2)-H(2)...O(1)#11	0.88	2.04	2.814(4)	145.8
	N(2)-H(2)...O(16)#11	0.88	2.54	3.043(6)	117.3
	N(4)-H(4)...O(3)#5	0.88	2.32	3.017(4)	136.7
	N(4)-H(4)...O(9)#5	0.88	2.55	3.335(4)	149.6
	O(13)-H(13A)...O(8)#10	0.85	2.13	2.967(4)	169.7
	O(13)-H(13A)...O(6)	0.85	2.56	3.064(4)	119
	O(13)-H(13B)...O(15)	0.85	2.05	2.852(6)	158.7
	O(14)-H(14A)...O(5)	0.85	2.00	2.852(5)	176.4
	O(14)-H(14A)...O(4)	0.85	2.64	3.052(5)	110.9
	O(14)-H(14B)...O(15)#4	0.85	2.25	2.915(8)	135
	O(14)-H(14B)...O(16)#4	0.85	2.54	3.095(8)	123.7
	O(15)-H(15B)...O(2)#4	0.85	2.38	2.922(6)	121.7
	O(16)-H(16B)...O(14)#4	0.85	2.38	3.095(8)	141
	O(16)-H(16B)...O(14)#10	0.85	2.39	2.995(8)	127.9
2	N(2)-H(2)...O(1)#12	0.88	2.04	2.810(3)	145.8
	N(2)-H(2)...O(16)#6	0.88	2.53	3.038(5)	117.2
	N(4)-H(4)...O(3)#5	0.88	2.3	3.005(3)	136.9
	N(4)-H(4)...O(9)#5	0.88	2.55	3.331(3)	148.9
	O(13)-H(13B)...O(6)	0.85	2.56	3.063(3)	119.4
	O(13)-H(13B)...O(8)#8	0.85	2.13	2.972(3)	169.3
	O(13)-H(13A)...O(15)#8	0.85	2.04	2.869(6)	165.3

	O(14)-H(14A)...O(4)	0.85	2.57	3.040(4)	115.8
	O(14)-H(14A)...O(5)	0.85	2.04	2.847(4)	158.2
	O(14)-H(14B)...O(16)#11	0.85	2.29	3.131(7)	169.9
	O(15)-H(15A)...O(2)#11	0.85	2.41	2.921(5)	119.4
	O(16)-H(16A)...O(14)	0.86	2.15	2.988(6)	168.1
	O(16)-H(16B)...O(2)#10	0.85	2.56	3.278(5)	143
3	N(2)-H(2)...O(1)#11	0.88	2	2.785(6)	147.6
	N(2)-H(2)...O(14)#11	0.88	2.62	3.105(9)	115.6
	N(4)-H(4)...O(3)#5	0.88	2.31	3.004(6)	135.6
	N(4)-H(4)...O(9)#5	0.88	2.52	3.314(6)	149.8
	O(13)-H(13A)...O(16)	0.85	2.08	2.832(8)	147.4
	O(13)-H(13B)...O(7)#10	0.85	2.17	2.986(5)	162
	O(13)-H(13B)...O(6)	0.85	2.47	3.066(5)	127.8
	O(15)-H(15A)...O(14)#12	0.85	2.17	3.017(11)	172.4
	O(15)-H(15B)...O(14)#9	0.85	2.22	2.992(11)	151.7
	O(16)-H(16A)...O(2)#3	0.85	2.18	2.906(9)	142.9
	O(16)-H(16B)...O(15)#13	0.85	2.35	2.935(12)	126.5

Symmetry code: for **1**, #4 -x+1, -y+1, -z+2; #5 -x, y+1/2, -z+3/2; #11 x+1, y+1, z; for **2**, #5 -x, y+1/2, -z+3/2; #6 x+1, y, z; #8 x, y-1, z; #10 x, y+1, z; #11 -x+1, -y+1, -z+2; #12 x+1, y+1, z; for **3**, #3 -x+1, -y+1, -z; #5 -x+2, y-1/2, -z+1/2; #9 -x+1, y-1/2, -z+1/2; #10 x, y+1, z; #11 x-1, y-1, z; #12 x, -y+3/2, z+1/2; #13 x, -y+3/2, z-1/2.

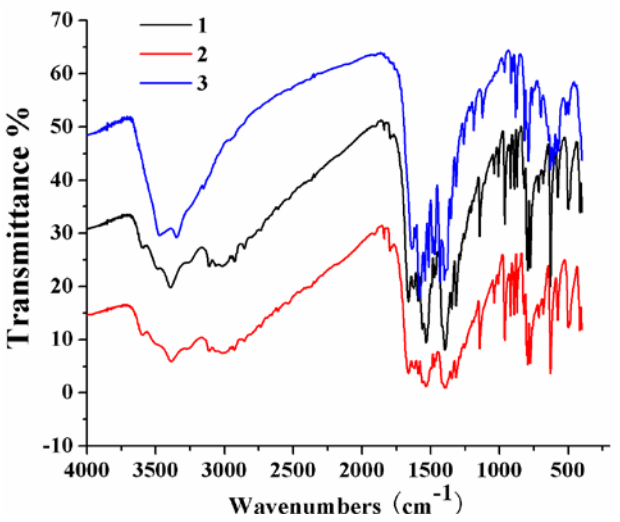


Fig. S1. The IR spectra of **1-3**.

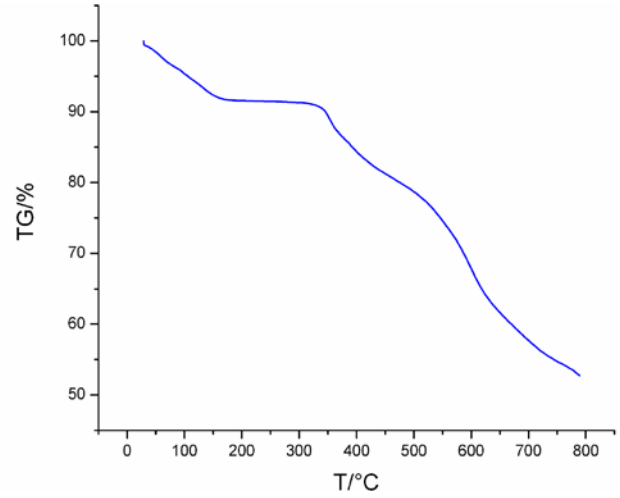
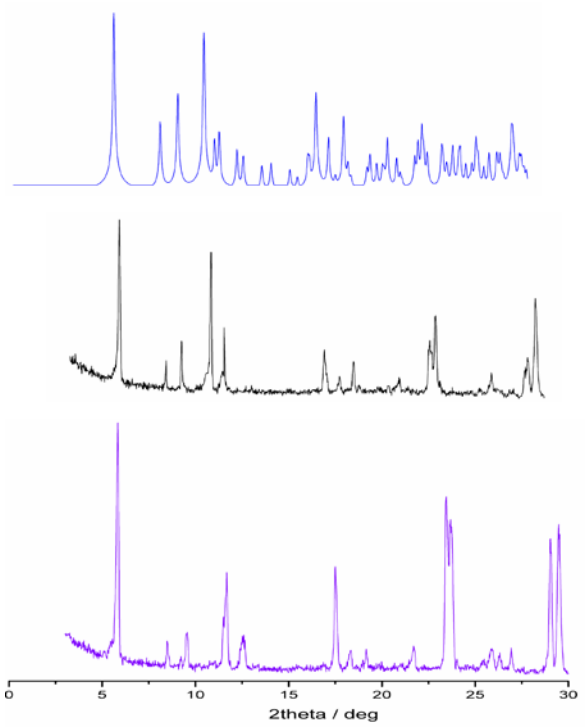
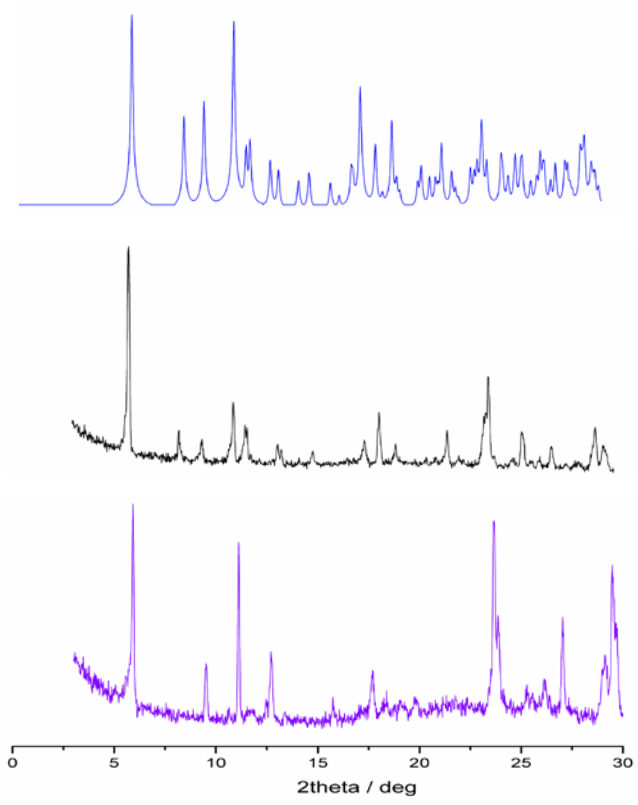


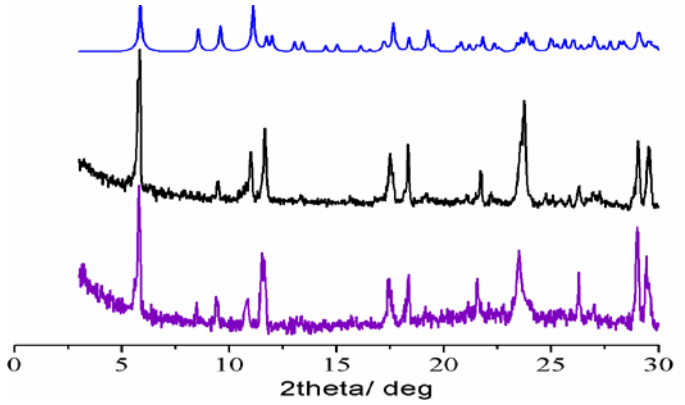
Fig. S2. TG curve of **3**.



(a)



(b)



(c)

Fig. S3 Powder XRD plots of (a) **1,** (b) **2,** (c) **3**: comparison of the XRD plots at room temperature (black), 180℃ (dehydration, violet) with the simulation pattern (blue).

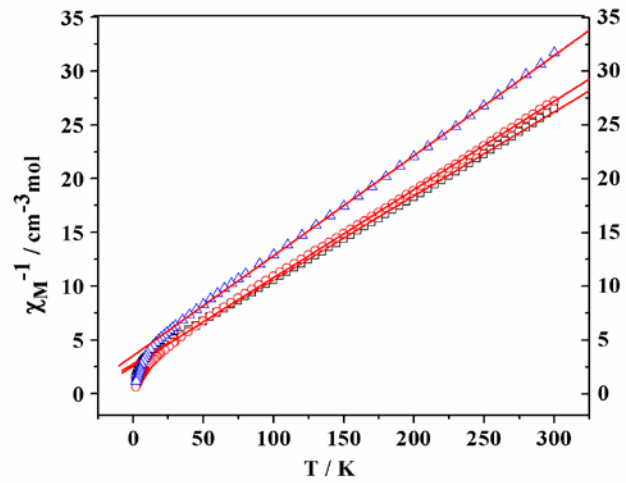


Fig. S4 χ_M^{-1} vs *T* curves for complexes **1** (black), **2** (red) and **3** (blue).