Supporting Information

Four new cobalt (II) coordination complexes: thermochromic switchable behavior in the process of dehydration and rehydration

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Figure S1. Stereo configurations and the core structures of the ligands (a) H_3L1 and (b) H_4L3.

Figure S2. Hydrogen bonding interactions in complex **3** between the adjacent layers along the *ac* plane. Green dotted lines represent the hydrogen bonds.

Figure S3. UV-vis diffuse reflectance spectroscopy for **1** (a), **2** (b), and **4** (c). Pink and orange solid lines: original complexes; purple dotted lines: dehydrated samples upon heating at 150 °C (**1** and **2**) and 180 °C (**4**); pink (**1** and **2**) and orange(**4**) dotted lines: rehydrated samples on exposure in the moist air. Insert: thermochromism of complexes **1**, **2** and **4**.

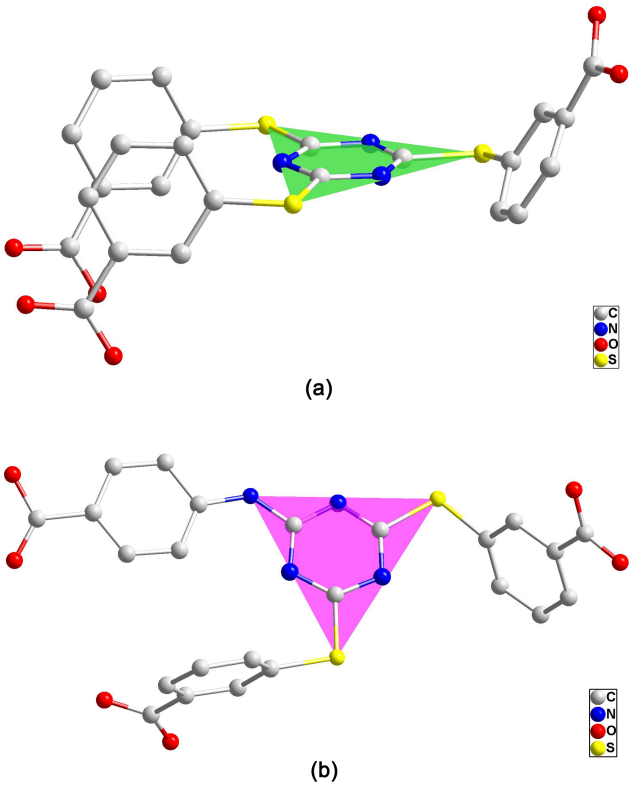
Figure S4. Powder X-ray diffraction patterns of complexes **1-4**. Black lines: simulated data of the original complexes; Red lines: original complexes at r. t., purple lines: dehydrated complexes upon heating at 150 °C (**1-3**) and 180 °C (**4**); pink (**1-3**) and orange (**4**) lines: rehydrated samples on exposure in the moist air.

Figure S5. FT-IR spectra for complex **1** (a), **2** (b), **3** (c) and **4** (d). Pink lines: original complexes at r. t.; purple lines: dehydrated complexes upon heating at 150 °C (**1-3**) and 180 °C (**4**); pink (**1-3**) and orange (**4**) lines: rehydrated samples on exposure in the moist air.

Figure S6. TGA curves for **1** (a), **2** (b), **3** (c) and **4** (d).

Table S1. Selected Bond Distances (Å) and Bond Angles (deg) for **1-4**.

Table S2. Hydrogen Bond Lengths (Å) and Bond Angles (°) for **2** and **3**.



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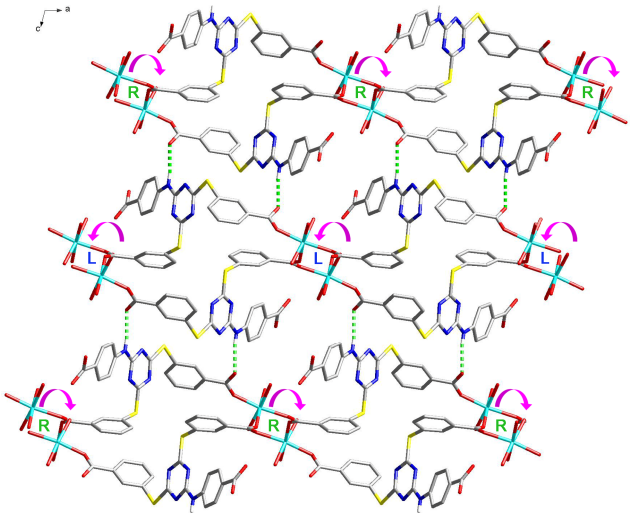

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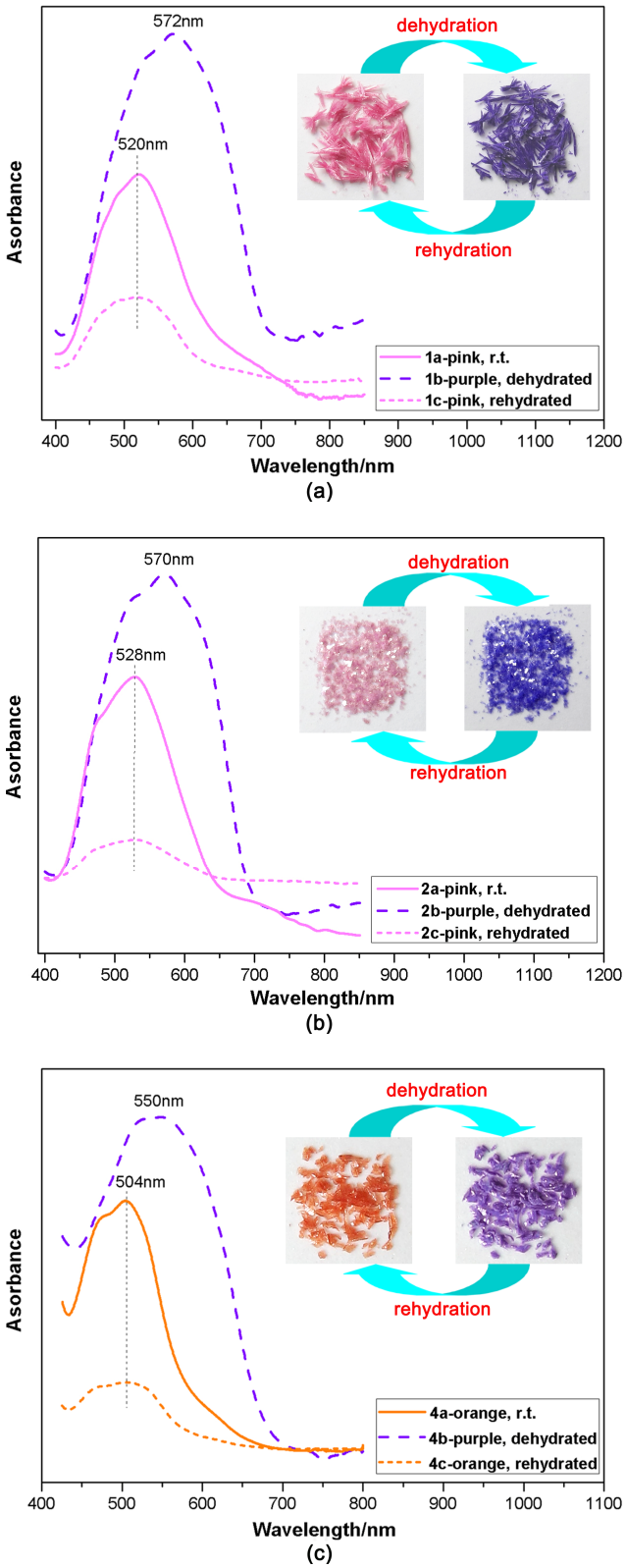
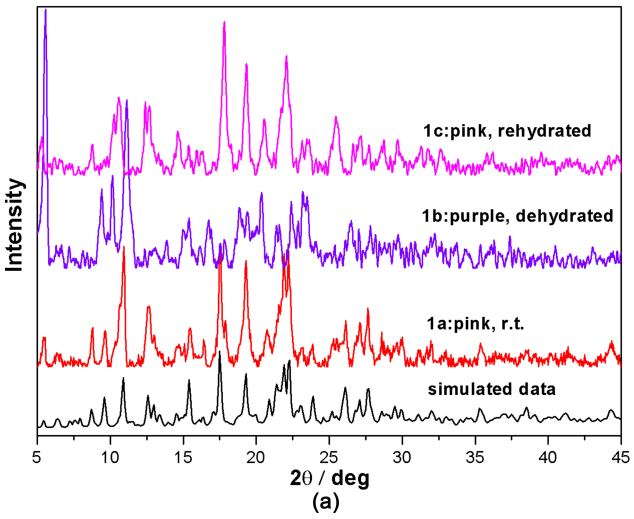
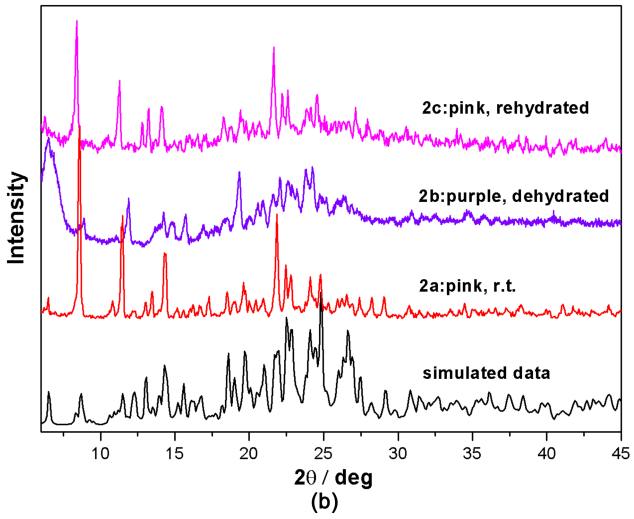


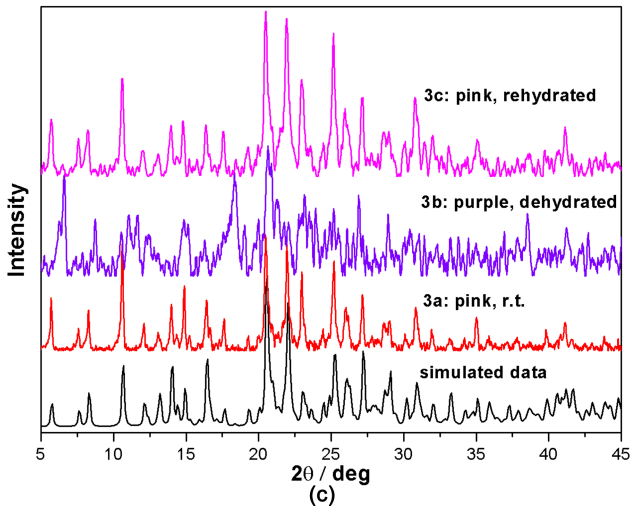
Figure **S3**. UV-vis diffuse reflectance spectroscopy for **1** (a), **2** (b), and **4** (c). Pink and orange solid lines: original complexes; purple dotted lines: dehydrated samples upon heating at 150 °C (**1** and **2**) and 180 °C (**4**); pink (**1** and **2**) and orange(**4**) dotted lines: rehydrated samples on exposure in the moist air. Insert: thermochromism of complexes **1**, **2** and **4**.



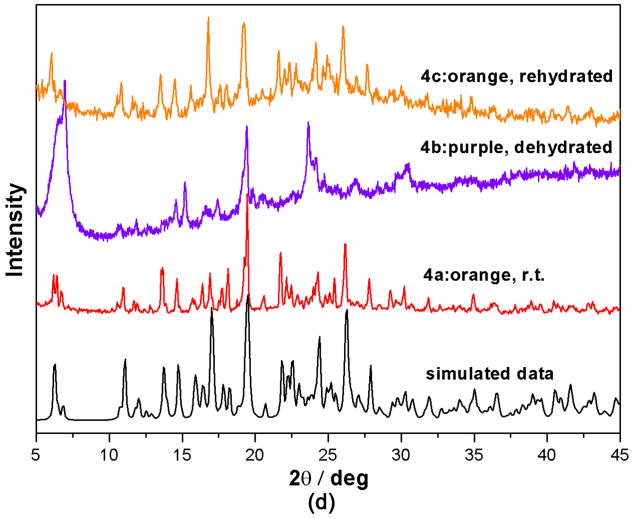
(a)



(b)



(c)



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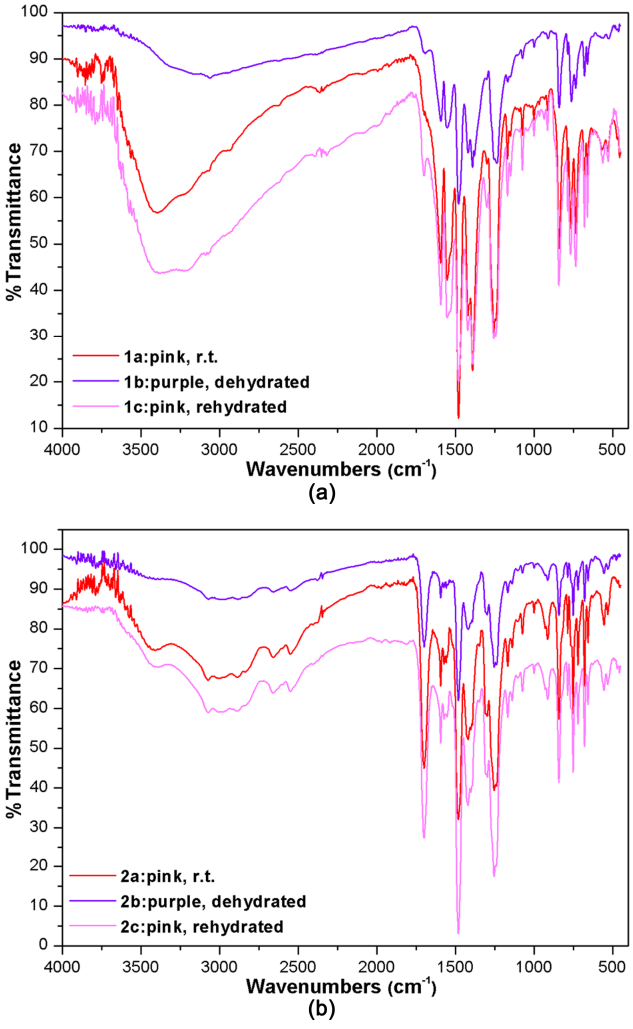


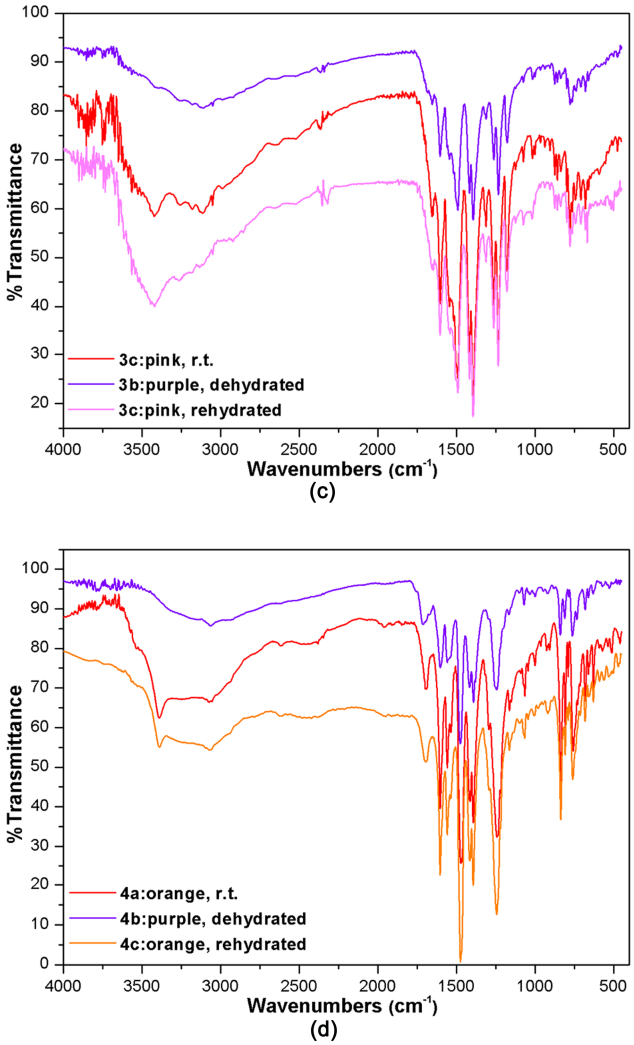
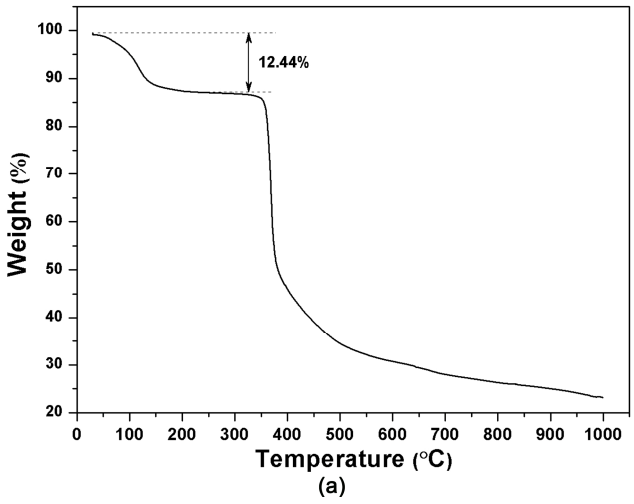
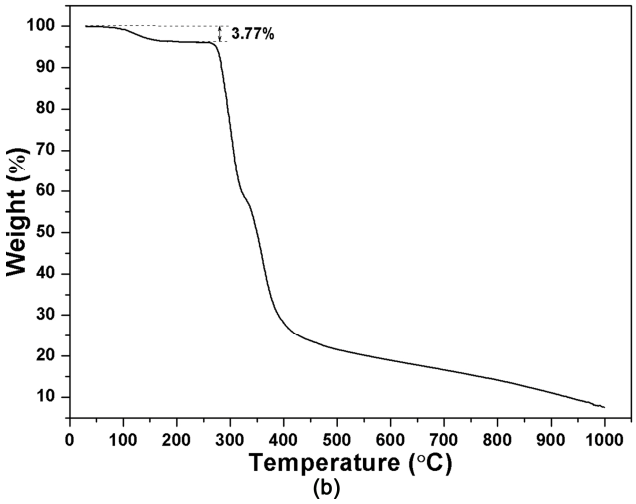
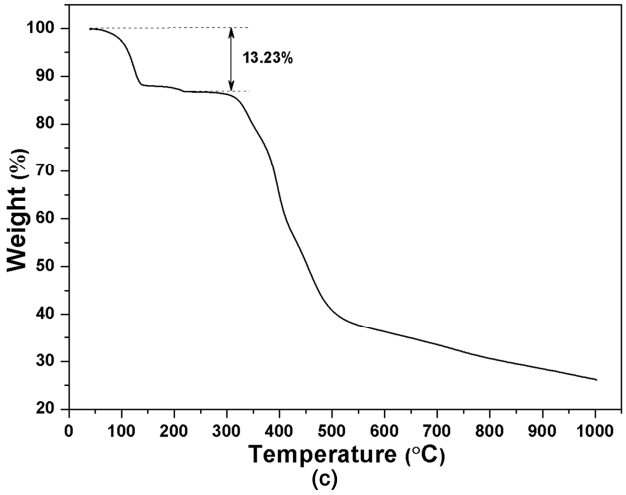


Figure S5. FT-IR spectra for complex **1** (a), **2** (b), **3** (c) and **4** (d). Red lines: original complexes at R. T., purple lines: dehydrated complexes upon heating at 150 °C (**1-3**) and 180 °C (**4**); pink (**1-3**) and orange (**4**) lines: rehydrated samples on exposure in the moist air.







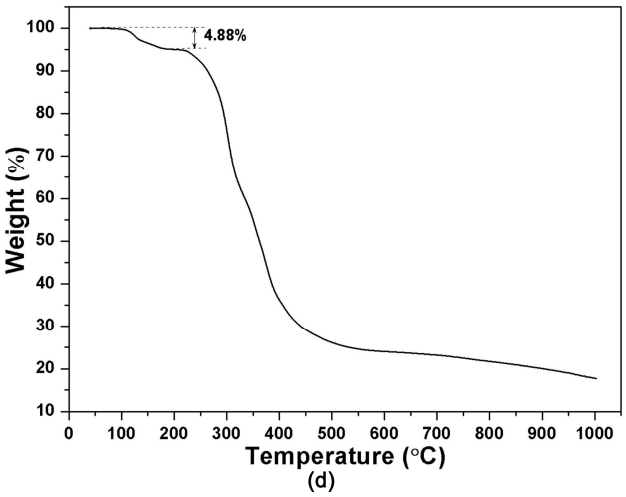


Figure S6. TGA curves for **1** (a), **2** (b), **3** (c) and **4** (d).

Table S1. Selected Bond Lengths [Å] and Angles [°] for Complex **1-4**[a].

1					
Co(1)-O(32)	2.047(5)	O(8)-Co(1)-O(1)	174.44(19)	O(19)-Co(4)-O(40)	91.6(3)
Co(1)-O(8)	2.054(4)	O(34)-Co(1)-O(1)	90.01(19)	O(17)-Co(4)-O(40)	86.9(2)
Co(1)-O(34)	2.104(5)	O(32)-Co(1)-O(31)	85.12(19)	O(5B)-Co(4)-O(41)	83.7(3)
Co(1)-O(1)	2.104(4)	O(8)-Co(1)-O(31)	88.13(19)	O(19)-Co(4)-O(41)	176.6(3)
Co(1)-O(31)	2.104(5)	O(34)-Co(1)-O(31)	94.4(2)	O(17)-Co(4)-O(41)	89.8(3)
Co(1)-O(33)	2.163(4)	O(1)-Co(1)-O(31)	93.27(18)	O(40)-Co(4)-O(41)	91.7(3)
Co(2)-O(7)	2.068(4)	O(32)-Co(1)-O(33)	93.99(18)	O(5B)-Co(4)-O(39)	92.7(2)
Co(2)-O(15)	2.077(5)	O(8)-Co(1)-O(33)	88.54(18)	O(19)-Co(4)-O(39)	88.3(3)
Co(2)-O(13)	2.090(4)	O(34)-Co(1)-O(33)	86.61(18)	O(17)-Co(4)-O(39)	90.9(2)
Co(2)-O(9)	2.096(4)	O(1)-Co(1)-O(33)	90.17(17)	O(40)-Co(4)-O(39)	177.8(2)
Co(2)-O(33)	2.099(4)	O(31)-Co(1)-O(33)	176.42(17)	O(41)-Co(4)-O(39)	88.3(3)
Co(2)-O(35)	2.133(4)	O(7)-Co(2)-O(15)	176.52(19)	O(19)-Co(4)-O(40)	91.6(3)
Co(3)-O(16)	2.016(4)	O(7)-Co(2)-O(13)	90.83(19)	O(6B) -Co(5)-O(20)	98.1(3)
Co(3)-O(21A)	2.052(4)	O(15)-Co(2)-O(13)	87.7(2)	O(6B) -Co(5)-O(3C)	169.9(2)
Co(3)-O(37)	2.073(5)	O(7)-Co(2)-O(9)	87.99(18)	O(20)-Co(5)-O(3C)	91.7(3)
Co(3)-O(36)	2.102(5)	O(15)-Co(2)-O(9)	93.49(19)	O(6B)-Co(5)-O(42)	86.5(3)
Co(3)-O(38)	2.149(5)	O(13)-Co(2)-O(9)	178.7(2)	O(20)-Co(5)-O(42)	85.3(3)
Co(3)-O(35)	2.181(4)	O(7)-Co(2)-O(33)	87.88(17)	O(3C)-Co(5)-O(42)	92.2(3)
Co(4)-O(5B)	2.040(5)	O(15)-Co(2)-O(33)	89.00(18)	O(6B)-Co(5)-O(3B)	89.7(3)
Co(4)-O(19)	2.069(8)	O(13)-Co(2)-O(33)	91.51(17)	O(20)-Co(5)-O(3B)	172.2(3)
Co(4)-O(17)	2.097(5)	O(9)-Co(2)-O(33)	88.97(17)	O(3C)-Co(5)-O(3B)	80.5(2)
Co(4)-O(40)	2.108(7)	O(7)-Co(2)-O(35)	92.94(17)	O(42)-Co(5)-O(3B)	96.0(3)
Co(4)-O(41)	2.156(9)	O(15)-Co(2)-O(35)	90.17(18)	O(6B)-Co(5)-O(39)	92.5(2)
Co(4)-O(39)	2.169(6)	O(13)-Co(2)-O(35)	88.12(17)	O(20)-Co(5)-O(39)	92.1(3)
Co(5)-O(6B)	2.016(7)	O(9)-Co(2)-O(35)	91.42(17)	O(3C)-Co(5)-O(39)	89.4(2)
Co(5)-O(20)	2.041(7)	O(16)-Co(3)-O(21A)	177.1(2)	O(42)-Co(5)-O(39)	177.0(4)
Co(5)-O(42)	2.139(8)	O(16)-Co(3)-O(37)	91.0(2)	O(3B)-Co(5)-O(39)	86.8(3)
Co(5)-O(3C)	2.107(7)	O(21A)-Co(3)-O(37)	90.1(2)	O(23)-Co(6)-O(23B)	180
Co(5)-O(3B)	2.143(6)	O(16)-Co(3)-O(36)	94.0(2)	O(23)-Co(6)-O(43B)	88.9(3)
Co(5)-O(39)	2.180(7)	O(21A)-Co(3)-O(36)	88.7(2)	O(23B)-Co(6)-O(43B)	91.1(3)
Co(6)-O(23)	1.964(8)	O(37)-Co(3)-O(36)	86.4(2)	O(23)-Co(6)-O(43)	91.1(3)
Co(6)-O(23B)	1.964(8)	O(16)-Co(3)-O(38)	82.3(2)	O(23B)-Co(6)-O(43)	88.9(3)
Co(6)-O(43B)	2.171(10)	O(21A)-Co(3)-O(38)	95.02(19)	O(43B)-Co(6)-O(43)	180
Co(6)-O(43)	2.171(10)	O(37)-Co(3)-O(38)	90.6(2)	O(23)-Co(6)-O(44B)	93.8(5)
Co(6)-O(44B)	2.191(11)	O(36)-Co(3)-O(38)	175.2(2)	O(23B)-Co(6)-O(44B)	86.2(5)
Co(6)-O(44)	2.191(11)	O(16)-Co(3)-O(35)	89.82(18)	O(43B)-Co(6)-O(44B)	86.4(4)
Co(1)-Co(2)	3.6947(12)	O(21A)-Co(3)-O(35)	89.12(17)	O(43)-Co(6)-O(44B)	93.6(4)
Co(2)-Co(3)	3.6876(12)	O(37)-Co(3)-O(35)	179.05(19)	O(23)-Co(6)-O(44)	86.2(5)
Co(4)-Co(5)	3.6042(10)	O(36)-Co(3)-O(35)	94.11(18)	O(23B)-Co(6)-O(44)	93.8(5)
Co(5)-Co(5D)	3.2430(8)	O(38)-Co(3)-O(35)	88.96(19)	O(43B)-Co(6)-O(44)	93.6(4)
O(32)-Co(1)-O(8)	97.4(2)	O(5B)-Co(4)-O(19)	97.0(3)	O(43)-Co(6)-O(44)	86.4(4)
O(32)-Co(1)-O(34)	178.0(2)	O(5B)-Co(4)-O(17)	172.5(2)	O(44B)-Co(6)-O(44)	180

O(8)-Co(1)-O(34)	84.5(2)	O(19)-Co(4)-O(17)	89.7(3)		
O(32)-Co(1)-O(1)	88.06(19)	O(5B)-Co(4)-O(40)	89.5(3)		
2					
Co(1)-O(7)	2.034(3)	O(13)-Co(1)-O(1W)	91.00(10)	O(8)-Co(2)-O(16)	94.71(12)
Co(1)-O(13)	2.088(3)	O(13)-Co(1)-O(1W)	91.00(10)	O(1)-Co(2)-O(16)	170.56(12)
Co(1)-O(2W)	2.116(4)	O(2W)-Co(1)-O(1W)	92.68(13)	O(4W)-Co(2)-O(16)	90.26(13)
Co(1)-O(3W)	2.121(3)	O(3W)-Co(1)-O(1W)	92.33(12)	O(15)-Co(2)-O(16)	60.29(11)
Co(1)-O(13A)	2.129(3)	O(7)-Co(1)-O(13)	176.78(13)	O(1W)-Co(2)-O(16)	92.23(11)
Co(1)-O(1W)	2.157(3)	O(7)-Co(1)-O(2W)	83.01(14)	O(8)-Co(2)-O(1)	94.53(13)
Co(2)-O(8)	2.004(3)	O(13)-Co(1)-O(2W)	93.79(13)	C(1)-S(1)-C(4)	102.4(2)
Co(2)-O(1)	2.057(3)	O(7)-Co(1)-O(3W)	96.45(12)	C(2)-S(2)-C(11)	102.4(2)
Co(2)-O(4W)	2.059(3)	O(13A)-Co(1)-O(1W)	170.89(11)	C(3)-S(3)-C(18)	104.3(2)
Co(2)-O(15)	2.081(3)	O(8)-Co(2)-O(1)	94.53(13)	C(31)-S(4)-C(34)	102.5(2)
Co(1)-Co(2)	3.7948(12)	O(8)-Co(2)-O(4W)	95.76(14)	C(32)-S(5)-C(41)	105.6(2)
Co(1)-Co(1A)	3.2219(12)	O(1)-Co(2)-O(4W)	86.94(14)	C(33)-S(6)-C(48)	102.6(2)
O(13)-Co(1)-O(3W)	86.77(12)	O(8)-Co(2)-O(15)	153.21(13)	C(61)-S(7)-C(64)	103.7(2)
O(2W)-Co(1)-O(3W)	174.95(13)	O(1)-Co(2)-O(15)	110.89(13)	C(62)-S(8)-C(71)	103.11(19)
O(7)-Co(1)-O(13A)	100.07(11)	O(4W)-Co(2)-O(15)	93.95(14)	C(63)-S(9)-C(78)	102.1(2)
O(13)-Co(1)-O(13A)	80.28(11)	O(8)-Co(2)-O(1W)	87.49(12)	C(91)-S(10)-C(94)	105.0(2)
O(2W)-Co(1)-O(13A)	90.54(13)	O(1)-Co(2)-O(1W)	90.05(12)	C(92)-S(11)-C(101)	105.1(2)
O(3W)-Co(1)-O(13A)	84.60(12)	O(4W)-Co(2)-O(1W)	175.73(13)	C(93)-S(12)-C(108)	103.6(2)
O(7)-Co(1)-O(1W)	88.79(11)	O(15)-Co(2)-O(1W)	84.29(12)		
3					
Co(1)-O(1)	2.055(3)	O(2W)-Co(1)-O(3A)	84.13(12)	O(2W)-Co(1)-O(1W)	176.32(11)
Co(1)-O(2W)	2.062(3)	O(1)-Co(1)-O(4B)	172.32(12)	O(3A)-Co(1)-O(1W)	94.60(12)
Co(1)-O(3A)	2.086(3)	O(2W)-Co(1)-O(4B)	97.90(11)	O(4B)-Co(1)-O(1W)	85.45(11)
Co(1)-O(4B)	2.111(3)	O(3A)-Co(1)-O(4B)	86.22(11)	O(3W)-Co(1)-O(1W)	89.51(13)
Co(1)-O(3W)	2.124(3)	O(1)-Co(1)-O(3W)	85.96(12)	C(3)-N(4)-C(18)	130.8(3)
Co(1)-O(1W)	2.153(3)	O(3A)-Co(1)-O(3W)	174.67(12)	C(1)-S(1)-C(4)	103.40(19)
O(1)-Co(1)-O(2W)	89.16(11)	O(4B)-Co(1)-O(3W)	90.73(11)	C(2)-S(2)-C(11)	101.84(19)
O(1)-Co(1)-O(3A)	97.59(11)	O(1)-Co(1)-O(1W)	87.59(11)		
4					
Co(1)-O(2W)	2.063(4)	O(2)-Co(1)-O(3)	89.91(14)	O(2W)-Co(1)-N(5)	90.50(16)
Co(1)-O(2)	2.082(3)	O(2W)-Co(1)-O(1W)	85.56(15)	O(2)-Co(1)-N(5)	175.21(15)
Co(1)-O(3)	2.085(4)	O(2)-Co(1)-O(1W)	87.28(12)	O(3)-Co(1)-N(5)	85.87(15)
Co(1)-O(1W)	2.126(3)	O(3)-Co(1)-O(1W)	93.16(14)	O(1W)-Co(1)-N(5)	90.70(14)
Co(1)-N(4)	2.147(3)	O(2W)-Co(1)-N(4)	90.98(15)	N(4)-Co(1)-N(5)	94.54(14)
Co(1)-N(5)	2.172(4)	O(2)-Co(1)-N(4)	87.75(12)	C(1)-S(1)-C(4)	101.4(3)
O(2W)-Co(1)-O(2)	93.67(15)	O(3)-Co(1)-N(4)	90.61(14)	C(2)-S(2)-C(11)	105.2(3)
O(2W)-Co(1)-O(3)	176.14(15)	O(1W)-Co(1)-N(4)	173.76(13)	C(3)-S(3)-C(18)	103.8(3)

[a]Symmetry codes for **1**: (A) -x, -y, -z; (B) 1-x, -y, -1-z; (C) -1+x, 1+y; z; (D) –x, 1-y, -1-z; for **2**: (A) -1-x, 1-y, -z; for **3**: (A) -x, -0.5+y, 1.5-z; (B) 1+x, -1+y, z.

Table S2. Hydrogen Bond Lengths (Å) and Bond Angles (°) for **2** and **3**.

2				
D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O4-H4A···O9i	0.82	1.81	2.612(6)	166
O6-H6A···O11ii	0.82	1.74	2.553(7)	170
O10-H10F···O3i	0.82	1.87	2.680(6)	168
O12-H12B···O5ii	0.82	1.87	2.686(6)	175
O18-H18A···O19iii	0.82	1.86	2.669(6)	171
O20-H20A···O17iv	0.82	1.80	2.600(7)	167
O22-H22B···O23v	0.82	1.86	2.673(6)	173
O24-H24A···O21v	0.82	1.84	2.650(6)	172
Symmetry codes: i -x, -y+1, -z+1; ii -x+1, -y+1, -z+1; iii x-1, y, z-1; iv x+1, y, z+1; v -x-1, -y, -z.				
3				
D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
N4-H4A···O2i	0.86	2.05	2.908(4)	172
O1W-H1WA···O2	0.85	1.82	2.633(4)	161
O1W-H1WB···O5ii	0.85	2.31	3.136(5)	165
O2W-H2WA···O4iii	0.85	1.85	2.695(4)	177
O2W-H2WB···O5iii	0.85	1.92	2.767(5)	177
O3W-H3WA···O3iv	0.85	2.29	2.856(4)	124
O3W-H3WB···O5Wv	0.85	1.87	2.719(5)	173
Symmetry codes: i -x, -y, -z+1; ii x+1, y-1, z; iii -x, y-3/2, -z+3/2; iv x+1, y-1, z; v x, y-1, z.				