Structural variation from Heterometallic Heptanuclear, Heptanuclear to Cubane Clusters based on 2-hydroxy-3-ethoxy-benzaldehyde : Effects of pH value and Temperature

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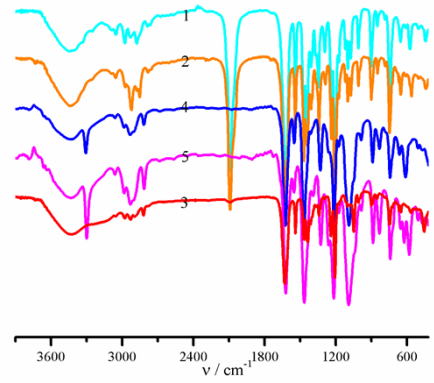


Figure S1. IR of **1-5**.

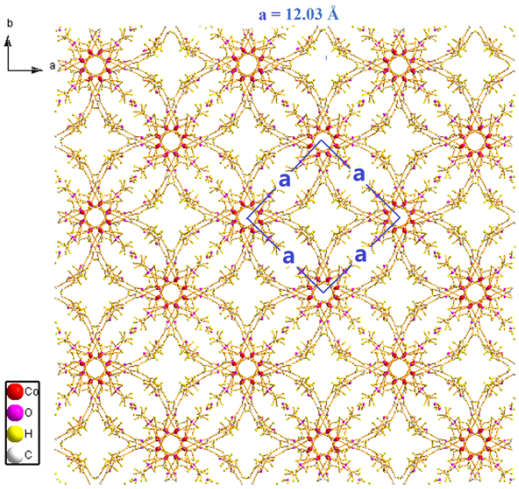


Figure S2. Packing drawing of **3**.

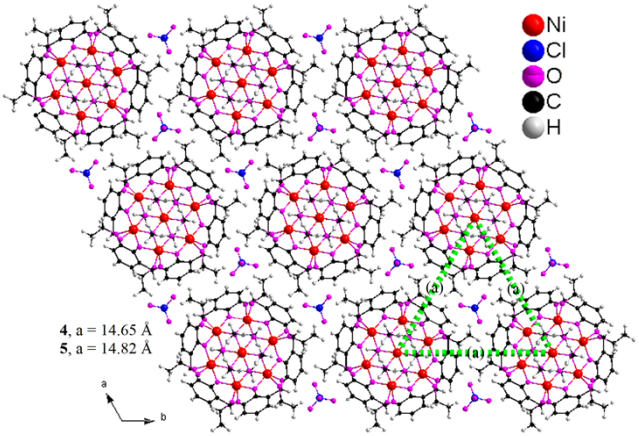


Figure S3. Packing drawing of **4** and **5**.

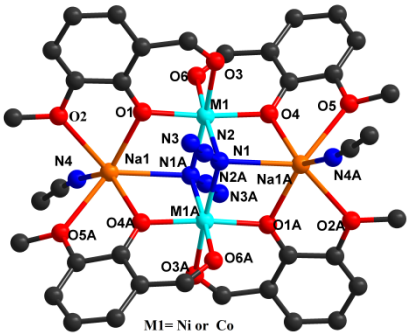
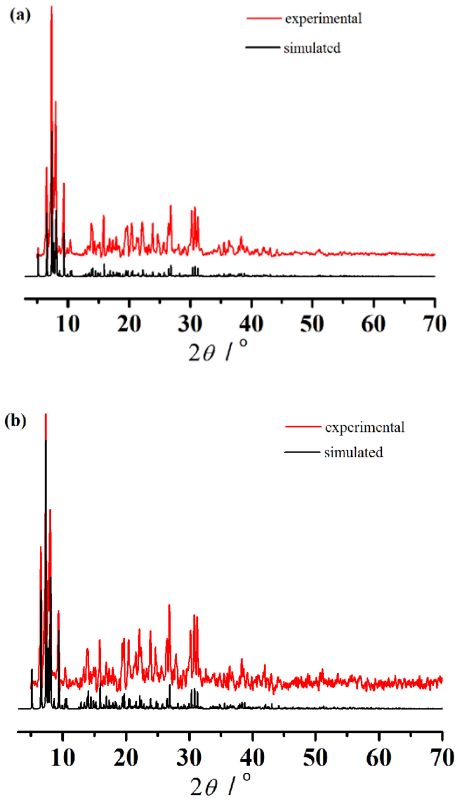


Figure S4. Structures of **a** and **b** where solvent molecules and all hydrogen atoms have been omitted for clarity.



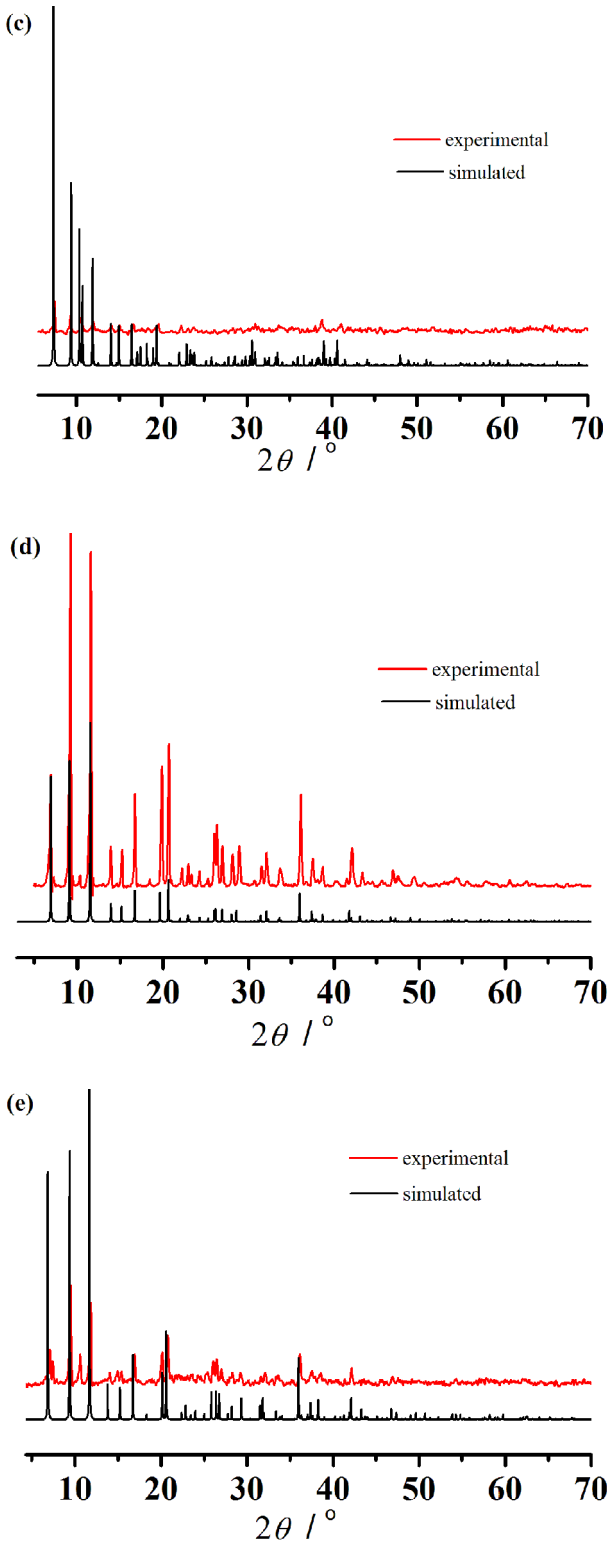


Figure S5. XRD and simulation XRD of **1** (a), **2** (b), **3** (c), **4** (d), and **5**(e).

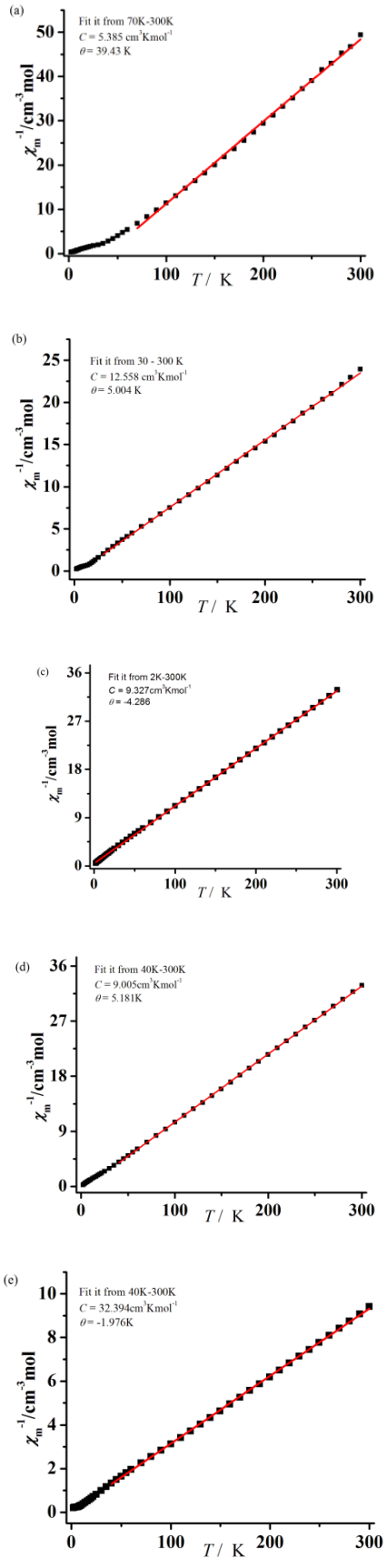
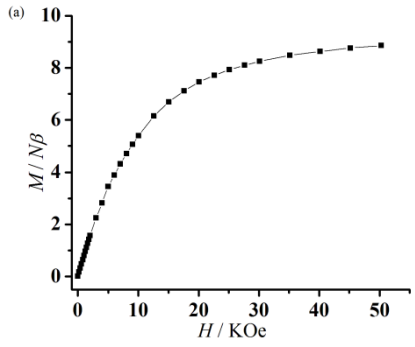
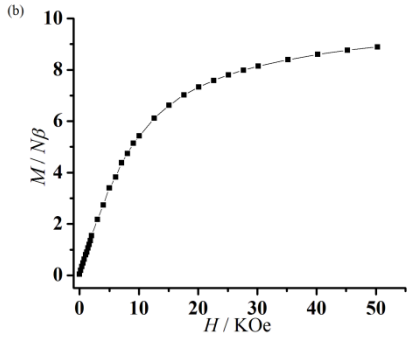
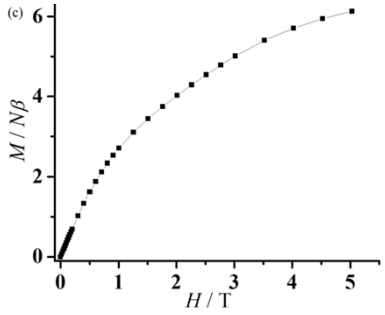
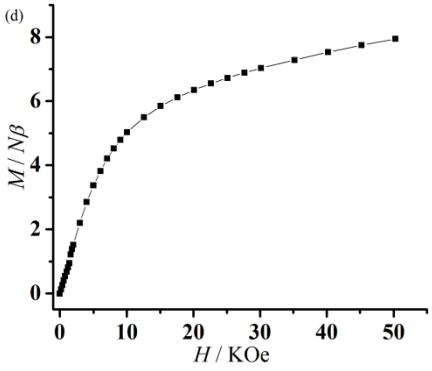


Figure S6. Plot of χ_M^{-1} *vs T* of **1** (a), **2** (b), **3** (c), **4** (d), and **5**(e). The solid lines represent the best fit.


(a)
M / Nβ
H / KOe


(b)
M / Nβ
H / KOe


(c)
M / Nβ
H / T


(d)
M / Nβ
H / KOe

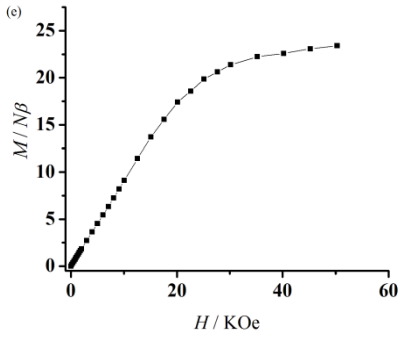
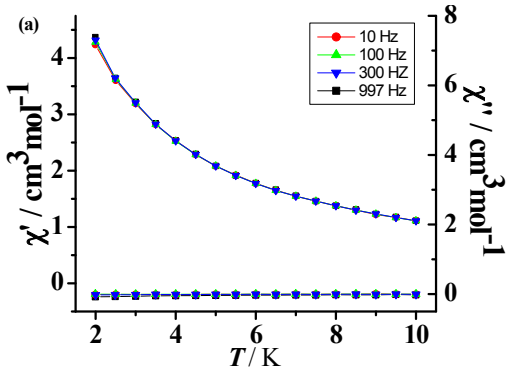
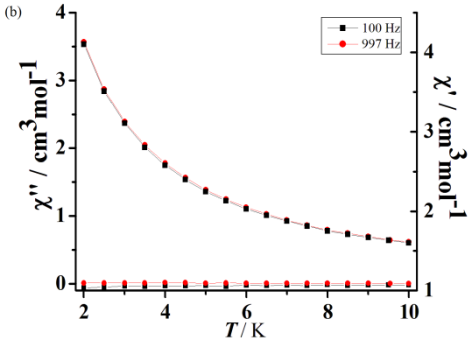
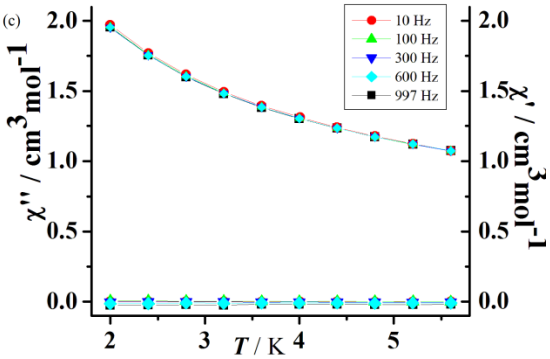


Figure S7. Field dependence of magnetization for **1** (a), **2** (b), **3** (c), **4** (d), and **5**(e) at 2 K.







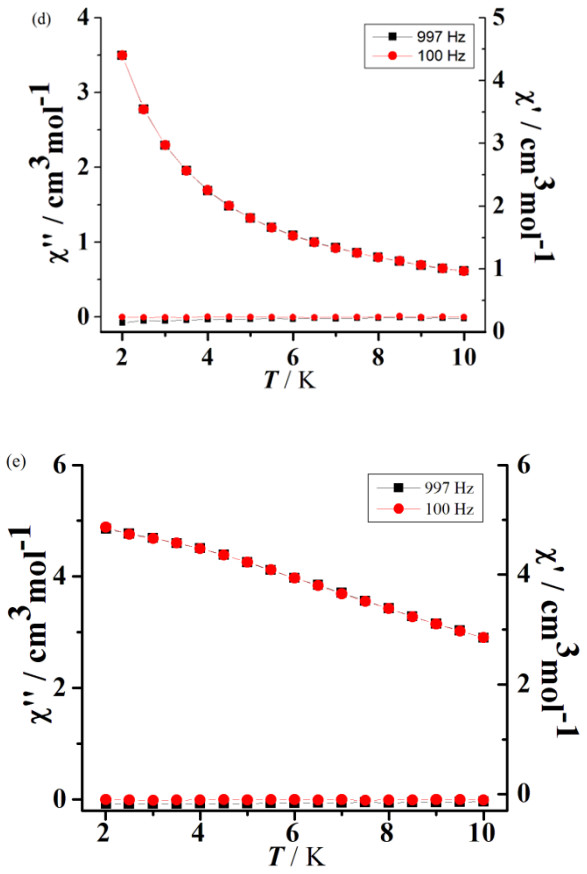


Figure S8. Curves of χ'' *and* χ' *vs T* of **1** (a), **2** (b), **3** (c), **4** (d), and **5**(e).

Table S1. Metal–Ligand Bond Lengths (Å) and Angles (°) in Complexes **1** and **2**.

Complexes[i]	**1**	**2**
N1-N2	1.180(5)	1.178(7)
N1-M2	2.096(4)	2.143(4)
N1-M1	2.127(4)	2.158(4)
N1-Na3	2.563(4)	2.548(5)
N2-N3	1.133(7)	1.142(8)
N4-N5	1.176(5)	1.170(6)
N4-M1	2.129(3)	2.165(4)
N4-M3	2.134(4)	2.187(4)
N4-Na1	2.551(4)	2.524(4)
N5-N6	1.146(6)	1.143(8)
N7-N8	1.175(5)	1.182(6)
N7-M4	2.113(3)	2.158(4)
N7-M1	2.138(4)	2.174(4)
N7-Na2	2.512(4)	2.498(5)
N8-N9	1.143(6)	1.136(8)
N10-N11	1.190(5)	1.193(6)
N10-M2	2.108(4)	2.145(4)

N10-M1	2.132(4)	2.167(4)
N10-Na1	2.563(4)	2.539(5)
N11-N12	1.126(6)	1.142(7)
N13-N14	1.192(5)	1.181(6)
N13-M1	2.107(3)	2.143(4)
N13-M4	2.108(4)	2.174(4)
N13-Na3	2.560(4)	2.538(5)
N14-N15	1.154(6)	1.143(7)
N16-N17	1.191(5)	1.194(6)
N16-M3	2.119(3)	2.155(4)
N16-M1	2.130(4)	2.179(4)
N16-Na2	2.548(4)	2.526(4)
N17-N18	1.142(6)	1.133(7)
Na1-O1	2.244(4)	2.277(4)
Na1-O16	2.251(4)	2.267(4)
Na1-O18	2.414(4)	2.403(4)
Na1-O3	2.470(4)	2.467(5)
Na2-O13	2.237(3)	2.259(4)
Na2-O10	2.252(3)	2.275(4)
Na2-O15	2.429(4)	2.427(5)
Na2-O12	2.451(4)	2.453(5)
Na3-O7	2.233(4)	2.246(4)
Na3-O4	2.237(4)	2.267(4)
Na3-O9	2.412(4)	2.390(5)
Na3-O6	2.453(4)	2.458(6)
M2-O1	2.005(3)	2.026(4)
M2-O4	2.020(3)	2.043(4)
M2-O2	2.050(4)	2.098(4)
M2-O5	2.061(4)	2.105(5)
M3-O13	1.992(3)	2.021(4)
M3-O16	2.009(3)	2.026(4)
M3-O14	2.047(3)	2.078(4)
M3-O17	2.055(4)	2.114(4)
M4-O10	1.999(3)	2.029(4)
M4-O7	2.019(3)	2.038(4)
M4-O11	2.039(3)	2.080(4)
M4-O8	2.062(4)	2.100(4)
N3-N2-N1	177.3(7)	176.3(8)
N6-N5-N4	176.4(6)	176.2(7)
N9-N8-N7	179.1(7)	179.2(9)
N12-N11-N10	177.0(6)	177.8(7)
N15-N14-N13	176.4(6)	176.0(7)
N18-N17-N16	177.3(6)	176.4(7)
O1-Na1-O16	160.17(14)	163.41(16)
O1-Na1-O18	124.00(15)	122.63(17)
O16-Na1-O18	67.43(13)	67.39(14)
O1-Na1-O3	67.20(13)	66.94(16)
O16-Na1-O3	126.98(14)	124.75(17)
O18-Na1-O3	110.73(14)	109.25(17)

O1-Na1-N4	91.87(14)	92.99(15)
O16-Na1-N4	72.82(13)	74.21(14)
O18-Na1-N4	139.09(15)	140.61(16)
O3-Na1-N4	100.46(14)	99.40(16)
O1-Na1-N10	72.92(13)	74.31(15)
O16-Na1-N10	90.29(13)	91.90(15)
O18-Na1-N10	97.18(13)	97.32(16)
O3-Na1-N10	139.44(14)	140.57(16)
N4-Na1-N10	73.35(12)	75.04(14)
O13-Na2-O10	162.87(16)	165.59(17)
O13-Na2-O15	67.56(12)	67.31(14)
O10-Na2-O15	125.60(14)	123.88(16)
O13-Na2-O12	121.11(14)	120.10(16)
O10-Na2-O12	67.87(12)	67.29(14)
O15-Na2-O12	109.05(15)	108.71(17)
O13-Na2-N7	93.69(14)	94.66(16)
O10-Na2-N7	73.50(13)	74.90(15)
O15-Na2-N7	102.67(14)	101.36(16)
O12-Na2-N7	139.57(13)	140.52(16)
O13-Na2-N16	72.49(12)	73.69(15)
O10-Na2-N16	92.93(13)	94.07(15)
O15-Na2-N16	139.81(13)	140.79(16)
O12-Na2-N16	94.82(14)	93.90(15)
N7-Na2-N16	75.40(13)	77.47(14)
O7-Na3-O4	161.66(15)	164.88(17)
O7-Na3-O9	67.95(14)	68.17(16)
O4-Na3-O9	124.91(17)	122.42(18)
O7-Na3-O6	125.55(15)	123.51(18)
O4-Na3-O6	66.74(14)	66.62(17)
O9-Na3-O6	106.05(15)	105.22(19)
O7-Na3-N13	72.86(13)	74.65(14)
O4-Na3-N13	92.33(14)	93.29(15)
O9-Na3-N13	140.52(16)	142.50(18)
O6-Na3-N13	100.24(14)	99.01(18)
O7-Na3-N1	91.23(14)	92.58(16)
O4-Na3-N1	73.66(13)	75.06(16)
O9-Na3-N1	103.26(14)	102.43(18)
O6-Na3-N1	139.47(15)	140.66(17)
N13-Na3-N1	72.53(13)	74.02(15)
N13-M1-N1	91.37(15)	90.79(17)
N13-M1-N4	171.86(16)	173.85(16)
N1-M1-N4	94.18(15)	93.52(16)
N13-M1-N16	95.15(14)	94.95(16)
N1-M1-N16	171.59(14)	172.81(16)
N4-M1-N16	79.92(14)	81.12(15)
N13-M1-N10	95.32(14)	94.28(16)
N1-M1-N10	79.25(15)	80.51(17)
N4-M1-N10	91.56(14)	90.76(16)
N16-M1-N10	94.83(14)	94.71(16)

N13-M1-N7	79.32(14)	81.04(16)
N1-M1-N7	93.49(15)	92.74(16)
N4-M1-N7	94.39(14)	94.36(16)
N16-M1-N7	92.93(15)	92.44(16)
N10-M1-N7	170.94(14)	171.78(16)
O1-M2-O4	176.35(15)	174.46(16)
O1-M2-O2	88.83(14)	86.98(18)
O4-M2-O2	89.12(15)	89.86(18)
O1-M2-O5	89.81(15)	90.16(19)
O4-M2-O5	87.34(15)	85.72(18)
O2-M2-O5	94.81(16)	97.22(19)
O1-M2-N1	93.99(15)	95.31(17)
O4-M2-N1	89.11(14)	89.27(16)
O2-M2-N1	92.15(16)	90.65(18)
O5-M2-N1	172.13(16)	170.65(19)
O1-M2-N10	88.37(13)	88.66(16)
O4-M2-N10	94.05(14)	95.12(17)
O2-M2-N10	171.93(15)	170.50(19)
O5-M2-N10	92.75(15)	91.23(17)
N1-M2-N10	80.50(14)	81.35(17)
O13-M3-O16	179.23(13)	178.54(16)
O13-M3-O14	88.69(13)	87.19(15)
O16-M3-O14	90.67(13)	91.46(16)
O13-M3-O17	91.34(15)	93.07(17)
O16-M3-O17	88.26(14)	86.42(16)
O14-M3-O17	91.79(15)	92.11(18)
O13-M3-N16	87.33(13)	87.04(15)
O16-M3-N16	93.36(14)	94.37(16)
O14-M3-N16	171.88(15)	171.30(17)
O17-M3-N16	95.38(14)	94.69(17)
O13-M3-N4	93.18(15)	93.80(16)
O16-M3-N4	87.28(13)	86.81(15)
O14-M3-N4	93.10(14)	92.73(17)
O17-M3-N4	173.42(15)	171.77(17)
N16-M3-N4	80.07(14)	81.17(15)
O10-M4-O7	177.15(12)	176.30(15)
O10-M4-O11	88.36(14)	86.85(16)
O7-M4-O11	89.26(14)	89.88(17)
O10-M4-O8	90.88(15)	92.47(17)
O7-M4-O8	87.72(14)	86.05(16)
O11-M4-O8	93.86(15)	94.38(18)
O10-M4-N13	93.97(15)	94.41(16)
O7-M4-N13	87.67(14)	87.35(15)
O11-M4-N13	91.78(15)	90.71(17)
O8-M4-N13	172.67(15)	171.65(18)
O10-M4-N7	88.00(14)	87.89(15)
O7-M4-N7	94.58(14)	95.62(16)
O11-M4-N7	170.65(14)	169.55(17)
O8-M4-N7	94.81(14)	94.86(17)

N13-M4-N7	79.88(14)	80.70(15)

i: (**1**)M = Ni; (**2**)M = Co

Table S2. Metal–Ligand Bond Lengths (Å) and Angles (°) in Complexes **3.**

Co1−O1	2.034(3)	Co1−O4^{ii}	2.122(3)
Co1−O4	2.061(3)	Co1−O5	2.156(4)
Co1−O2	2.069(4)	Co1−O4^{i}	2.080(3)
O1−Co1−O4	172.62(14)	O2−Co1−O5	88.15(16)
O1−Co1−O2	88.11(13)	O4^{i}−Co1−O5	89.74(14)
O4−Co1−O2	94.25(13)	O2−Co1−O4^{ii}	99.01(15)
O1−Co1−O4^{i}	93.50(13)	O4^{i}−Co1−O4^{ii}	82.87(13)
O4−Co1−O4^{i}	84.38(13)	O1−Co1−O5	96.67(16)
O2−Co1−O4^{i}	177.48(15)	O4−Co1−O5	90.41(15)
O1−Co1−O4^{ii}	92.27(13)	O4^{ii}−Co1−O5	168.73(14)
O4−Co1−O4^{ii}	80.45(15)	Co1−O4−Co1^{iii}	96.51(13)
Co1−O4−Co1^{ii}	99.49(14)	Co1^{iii}−O4−Co1^{ii}	94.65(13)

Symmetry codes: (i) −*y*+1, *x*+1/2, −*z*+1; (ii) −*x*+1/2, −*y*+3/2, *z*; (iii) *y*−1/2, −*x*+1, −*z*+1.

Table S3. Metal–Ligand Bond Lengths (Å) and Angles (°) in Complex **4**.

Ni1-O1^{i}	1.990(4)	Ni1-O4	2.076(4)
Ni1-O1	1.997(3)	Ni1-O3	2.345(4)
Ni1-O2^{i}	2.029(5)	Ni1-O4^{ii}	2.045(4)
Ni2-O4	2.077(3)	O1-Ni1-O4	95.94(16)
O1^{i}-Ni1-O1	172.78(9)	O2^{i}-Ni1-O4	166.69(18)
O1^{i}-Ni1-O2^{i}	87.44(18)	O4^{ii}-Ni1-O4	83.0(2)
O1-Ni1-O2^{i}	97.35(18)	O1^{i}-Ni1-O3	102.43(15)
O1^{i}-Ni1-O4^{ii}	104.70(16)	O1-Ni1-O3	72.44(15)
O1-Ni1-O4^{ii}	79.85(15)	O2^{i}-Ni1-O3	88.27(18)
O2^{i}-Ni1-O4^{ii}	100.13(19)	O4^{ii}-Ni1-O3	151.87(15)
O1^{i}-Ni1-O4	79.26(15)	O4-Ni1-O3	95.03(16)
O4^{i}-Ni2-O4	82.17(15)	O4^{ii}-Ni2-O4^{iv}	82.17(15)
O4^{ii}-Ni2-O4^{i}	97.83(15)	O4^{i}-Ni2-O4^{iv}	180.00(10)
O4-Ni2-O4^{vi}	180.000(1)	Ni1^{i}-O4-Ni1	98.07(16)
Ni1^{ii}-O1-Ni1	102.61(16)	Ni1^{i}-O4-Ni2	97.77(16)
O4^{iii}-Ni2-O4^{ii}	180.00(17)	Ni1-O4-Ni2	96.81(17)

Symmetry codes: (i) $x-y, x, -z+2$; (ii) $y, -x+y, -z+2$; (iii) $-y, x-y, z$; (iv) $-x+y, -x, z$.

Table S4. Metal–Ligand Bond Lengths (Å) and Angles (°) in Complex **5**.

Co1-O1	2.021(4)	Co1-O4	2.108(4)
Co1-O1^{i}	2.029(4)	O1^{i}-Co1-O4	79.00(14)
Co1-O2^{i}	2.062(5)	O2^{i}-Co1-O4	165.28(17)
Co2-O4	2.129(4)	O4^{ii}-Co1-O4	84.0(2)
O1-Co1-O1^{i}	171.78(9)	O1-Co1-O3	71.49(14)
O1-Co1-O2^{i}	99.220(18)	O1^{i}-Co1-O3	103.06(15)
O1^{i}-Co1-O2^{i}	86.37(17)	O2^{i}-Co1-O3	86.12(18)
O1-Co1-O4^{ii}	79.90(15)	O4^{ii}-Co1-O3	151.24(15)
O1^{i}-Co1-O4^{ii}	105.04(16)	O4-Co1-O3	95.56(16)
O2^{i}-Co1-O4^{ii}	101.54(18)	O1-Co1-O4	95.19(16)
O4-Co2-O4^{i}	82.26(14)	Co1-O1-Co1^{ii}	102.82(14)
O4^{ii}-Co2-O4^{i}	97.74(14)	Co1^{i}-O4-Co1	98.13(16)
O4^{iv}-Co2-O4	180.00(18)	Co1^{i}-O4-Co2	97.14(16)
O4^{iii}-Co2-O4^{i}	82.29(13)	Co1-O4-Co2	96.23(16)
O4^{iii}-Co2-O4^{ii}	180.000(17)		

Symmetry codes: (i) *y*, −*x*+*y*, −*z*+1; (ii) *x*−*y*, *x*, −*z*+1; (iii) −*x*+*y*, −*x*, *z*; (iv) −*x*, −*y*, −*z*+1.

Table S5. Hydrogen Bond Lengths (Å) and Angles (°) in Complexes **1.**

D-H···*A*	*D*-H	H···*A*	*D*···*A*	*D*-H···*A*
N19-H19A···N6^{i}	0.91	2.02	2.934(9)	176.8

Symmetry codes: (i) *x*−1, *y*, *z*.

Table S6. Hydrogen Bond Lengths (Å) and Angles (°) in Complexes **2**

D-H···*A*	*D*-H	H···*A*	*D*···*A*	*D*-H···*A*
N19-H19A···N6^{i}	0.91	2.02	2.929(12)	178.0

Symmetry codes: (i) *x*−1, *y*, *z*.

Table S7. Hydrogen Bond Lengths (Å) and Angles (°) in Complexes **3**.

D-H···*A*	*D*-H	H···*A*	*D*···*A*	*D*-H···*A*
O5-H5B···O1^{iii}	0.93	1.92	2.764(5)	149.7
O5-H5B···O3^{iii}	0.93	2.58	3.302(6)	134.3

Symmetry codes: (iii) *y*−1/2, −*x*+1, −*z*+1.