

Supporting Information

Synthesis, structure and magnetism of a novel series of trinuclear nickel(II) clusters

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Table S1. Selected bond lengths (Å) and angles (°) parameters for **1**.

Selected bond lengths			
Ni2—O4	2.038(5)	Ni1—O1	1.860(5)
Ni2—O3	2.051(5)	Ni1—O2	1.817(5)
Ni2—N3	2.004(6)	Ni1—N2	1.832(6)
Ni2—N6	2.038(6)	Ni1—N1	1.930(6)
Ni2—N4	2.134(7)	Ni4—O7	2.041(5)
Ni2—N5	2.129(7)	Ni4—O7 ⁱ	2.041(5)
Ni3—O5	1.874(6)	Ni4—N11	2.044(6)
Ni3—O6	1.828(6)	Ni4—N11 ⁱ	2.044(6)
Ni3—N7	1.817(6)	Ni4—N9 ⁱ	2.139(8)
Ni3—N8	1.940(7)	Ni4—N9	2.139(8)
Ni5—O9	1.856(5)	Ni5—N10	1.824(6)
Ni5—O8	1.822(6)	Ni5—N12	1.938(6)
Selected bond angle			
O3—Ni2—N4	89.9(2)	O7 ⁱ —Ni4—N11	101.0(2)
O3—Ni2—N5	88.9(2)	O7—Ni4—N11 ⁱ	101.0(2)
O4—Ni2—O3	176.7(2)	O7 ⁱ —Ni4—N9 ⁱ	91.6(2)
O4—Ni2—N6	79.0(2)	O7—Ni4—N9 ⁱ	88.4(2)
O4—Ni2—N4	91.3(2)	O7 ⁱ —Ni4—N9	88.4(2)
O4—Ni2—N5	90.1(2)	O7—Ni4—N9	91.6(2)
N3—Ni2—O3	79.6(2)	N11—Ni4—N11 ⁱ	180.0
N3—Ni2—O4	97.2(2)	N11—Ni4—N9	89.8(3)
N3—Ni2—N6	176.2(3)	N11 ⁱ —Ni4—N9	90.2(3)
N3—Ni2—N4	91.4(3)	N11 ⁱ —Ni4—N9 ⁱ	89.8(3)
N3—Ni2—N5	90.9(2)	N11—Ni4—N9 ⁱ	90.2(3)
N6—Ni2—O3	104.1(2)	N9 ⁱ —Ni4—N9	180.0(4)
N6—Ni2—N4	88.1(3)	O9—Ni5—N12	91.3(3)
N6—Ni2—N5	89.8(2)	O8—Ni5—O9	178.0(3)
N5—Ni2—N4	177.1(3)	O8—Ni5—N10	93.8(2)
O2—Ni1—O1	179.2(2)	O8—Ni5—N12	90.1(3)
O2—Ni1—N2	94.7(2)	N10—Ni5—O9	84.7(2)
O2—Ni1—N1	90.2(3)	N10—Ni5—N12	176.0(3)
O1—Ni1—N1	90.5(3)	O5—Ni3—N8	91.6(3)
N2—Ni1—O1	84.6(2)	O6—Ni3—O5	177.0(3)
N2—Ni1—N1	174.8(3)	O6—Ni3—N8	89.8(3)
O7 ⁱ —Ni4—O7	180.0	N7—Ni3—O5	83.8(3)
O7 ⁱ —Ni4—N11 ⁱ	79.0(2)	N7—Ni3—O6	94.9(3)
O7—Ni4—N11	79.0(2)	N7—Ni3—N8	175.1(3)

Symmetry code: (i) -x+1, -y+1, -z+1.

Table S2. Selected bond lengths (Å) and angles (°) parameters for **2**.

Selected bond lengths			
Ni1—O1	1.857(4)	Ni2—N4	2.117(4)
Ni1—N2	1.825(4)	Ni2—N4 ⁱⁱ	2.117(4)
Ni1—O2	1.814(4)	Ni2—O3	2.030(3)
Ni1—N1	1.915(5)	Ni2—O3 ⁱⁱ	2.030(3)
Ni1—O1	1.857(4)	Ni2—N3	2.050(4)
Ni1—N2	1.825(4)	Ni3—O5	1.867(3)
Ni1—O2	1.814(4)	Ni3—O4	1.814(3)
Ni1—N1	1.915(5)	Ni3—N7	1.827(4)
Ni1—O1	1.857(4)	Ni3—N6	1.929(4)
Ni1—N2	1.825(4)	Ni4—O6	2.049(3)
Ni1—O2	1.814(4)	Ni4—O6 ⁱ	2.049(3)
Ni2—O3	2.030(3)	Ni4—N8 ⁱ	2.046(4)
Ni2—O3 ⁱⁱ	2.030(3)	Ni4—N8	2.046(4)
Ni2—N3	2.050(4)	Ni4—N9	2.109(4)
Ni2—N3 ⁱⁱ	2.050(4)	Ni4—N9 ⁱ	2.109(4)
Selected bond angles			
O6 ⁱ —Ni4—O6	180.00(17)	O3—Ni2—N4	90.44(14)
O6—Ni4—N9 ⁱ	90.28(14)	O3 ⁱⁱ —Ni2—N4	89.56(14)
O6 ⁱ —Ni4—N9 ⁱ	89.72(14)	O3—Ni2—N4 ⁱⁱ	89.56(14)
O6 ⁱ —Ni4—N9	90.28(14)	N3 ⁱⁱ —Ni2—N3	180.00(19)
O6—Ni4—N9	89.72(14)	N3 ⁱⁱ —Ni2—N4	91.23(16)
N8 ⁱ —Ni4—O6	101.21(14)	N3—Ni2—N4	88.77(16)
N8—Ni4—O6 ⁱ	101.20(14)	N3 ⁱⁱ —Ni2—N4 ⁱⁱ	88.77(16)
N8 ⁱ —Ni4—O6 ⁱ	78.79(14)	N3—Ni2—N4 ⁱⁱ	91.23(16)
N8—Ni4—O6	78.80(14)	N4—Ni2—N4 ⁱⁱ	180.0(2)
N8—Ni4—N8 ⁱ	180.0	O5—Ni3—N6	91.76(16)
N8—Ni4—N9	89.96(16)	O4—Ni3—O5	177.12(17)
N8—Ni4—N9 ⁱ	90.04(16)	O4—Ni3—N7	94.65(16)
N8 ⁱ —Ni4—N9	90.04(16)	O4—Ni3—N6	89.59(17)
N8 ⁱ —Ni4—N9 ⁱ	89.96(16)	N7—Ni3—O5	84.17(15)
N9—Ni4—N9 ⁱ	180.0(2)	N7—Ni3—N6	174.28(17)
O3—Ni2—O3 ⁱⁱ	180.0	O1—Ni1—N1	92.4(2)
O3—Ni2—N3 ⁱⁱ	100.52(15)	N2—Ni1—O1	84.51(17)
O3 ⁱⁱ —Ni2—N3 ⁱⁱ	79.48(15)	N2—Ni1—N1	175.2(2)
O3—Ni2—N3	79.48(15)	O2—Ni1—O1	176.98(18)
O3 ⁱⁱ —Ni2—N3	100.52(15)	O2—Ni1—N2	94.7(2)
O3 ⁱⁱ —Ni2—N4 ⁱⁱ	90.44(14)	O2—Ni1—N1	88.5(2)

Symmetry code: (i) -x, -y+2, -z+2; (ii) -x+1, -y+2, -z+1.

TableS3. Selected bond lengths (Å) and angles (°) parameters for **3**.

Selected bond lengths			
Ni1—O2	1.821(4)	Ni4—O4 ⁱ	2.038(3)
Ni1—O1	1.855(4)	Ni4—O4	2.038(3)
Ni1—N3	1.828(4)	Ni4—N7 ⁱ	2.038(4)
Ni1—N4	1.940(4)	Ni4—N7	2.038(4)
Ni2—O3	2.039(3)	Ni4—N8 ⁱ	2.112(4)
Ni2—O3 ⁱⁱ	2.039(3)	Ni4—N8	2.112(4)
Ni2—N2	2.042(4)	Ni3—O6	1.859(4)
Ni2—N2 ⁱⁱ	2.042(4)	Ni3—O5	1.817(4)
Ni2—N1 ⁱⁱ	2.117(5)	Ni3—N6	1.833(4)
Ni2—N1	2.117(5)	Ni3—N5	1.921(4)
Selected bond angle			
O2—Ni1—O1	176.91(17)	O4—Ni4—O4 ⁱ	180.0
O2—Ni1—N3	94.52(17)	O4—Ni4—N8	89.61(14)
O2—Ni1—N4	90.47(17)	O4 ⁱ —Ni4—N8	90.39(14)
O1—Ni1—N4	90.89(17)	O4 ⁱ —Ni4—N8 ⁱ	89.61(14)
N3—Ni1—O1	84.30(17)	O4—Ni4—N8 ⁱ	90.39(14)
N3—Ni1—N4	173.9(2)	N7—Ni4—O4 ⁱ	100.49(14)
O3 ⁱⁱ —Ni2—O3	180.0	N7 ⁱ —Ni4—O4	100.49(14)
O3—Ni2—N2 ⁱⁱ	100.65(15)	N7 ⁱ —Ni4—O4 ⁱ	79.51(14)
O3—Ni2—N2	79.35(15)	N7—Ni4—O4	79.51(14)
O3 ⁱⁱ —Ni2—N2 ⁱⁱ	79.36(15)	N7—Ni4—N7 ⁱ	180.0
O3 ⁱⁱ —Ni2—N2	100.65(15)	N7—Ni4—N8 ⁱ	91.05(15)
O3—Ni2—N1 ⁱⁱ	90.46(16)	N7 ⁱ —Ni4—N8 ⁱ	88.95(15)
O3 ⁱⁱ —Ni2—N1 ⁱⁱ	89.54(16)	N7—Ni4—N8	88.95(15)
O3 ⁱⁱ —Ni2—N1	90.46(16)	N7 ⁱ —Ni4—N8	91.05(15)
O3—Ni2—N1	89.54(16)	N8—Ni4—N8 ⁱ	180.0
N2—Ni2—N2 ⁱⁱ	180.00(10)	O6—Ni3—N5	91.51(17)
N2 ⁱⁱ —Ni2—N1 ⁱⁱ	86.99(17)	O5—Ni3—O6	178.71(15)
N2—Ni2—N1	87.00(17)	O5—Ni3—N6	94.18(17)
N2—Ni2—N1 ⁱⁱ	93.00(17)	O5—Ni3—N5	89.75(18)
N2 ⁱⁱ —Ni2—N1	93.01(17)	N6—Ni3—O6	84.56(16)
N1 ⁱⁱ —Ni2—N1	180.0	N6—Ni3—N5	175.65(19)

Symmetry code: (i) $-x, -y+2, -z+1$; (ii) $-x+1, -y+2, -z$.

TableS4. Selected bond lengths (Å) and angles (°) parameters for **4**.

Selected bond lengths			
Ni1—O2	1.826(3)	Ni3—O7 ⁱ	2.042(3)
Ni1—O1	1.846(3)	Ni3—O7	2.042(3)
Ni1—N6	1.826(4)	Ni3—N2	2.036(3)
Ni1—N7	1.938(4)	Ni3—N2 ⁱ	2.036(3)
Ni2—O3	2.046(3)	Ni3—N3	2.110(4)
Ni2—O3 ⁱⁱ	2.046(3)	Ni3—N3 ⁱ	2.110(4)
Ni2—N8 ⁱⁱ	2.120(4)	Ni4—O5	1.861(3)
Ni2—N8	2.120(4)	Ni4—O6	1.817(3)
Ni2—N5	2.030(4)	Ni4—N1	1.833(3)
Ni2—N5 ⁱⁱ	2.030(4)	Ni4—N4	1.921(4)
Selected bond angle			
O2—Ni1—O1	177.62(15)	O7—Ni3—O7 ⁱ	180.0
O2—Ni1—N7	90.81(15)	O7—Ni3—N3	91.00(13)
O1—Ni1—N7	90.43(15)	O7 ⁱ —Ni3—N3	89.00(13)
N6—Ni1—O2	94.39(15)	O7 ⁱ —Ni3—N3 ⁱ	91.00(13)
N6—Ni1—O1	84.49(15)	O7—Ni3—N3 ⁱ	89.00(13)
N6—Ni1—N7	173.99(17)	N2 ⁱ —Ni3—O7 ⁱ	79.25(13)
O3 ⁱⁱ —Ni2—O3	180.0	N2—Ni3—O7	79.25(13)
O3—Ni2—N8 ⁱⁱ	89.14(14)	N2—Ni3—O7 ⁱ	100.75(13)
O3—Ni2—N8	90.86(14)	N2 ⁱ —Ni3—O7	100.75(13)
O3 ⁱⁱ —Ni2—N8	89.14(14)	N2 ⁱ —Ni3—N2	180.0
O3 ⁱⁱ —Ni2—N8 ⁱⁱ	90.86(14)	N2—Ni3—N3 ⁱ	88.90(14)
N8—Ni2—N8 ⁱⁱ	180.0	N2 ⁱ —Ni3—N3 ⁱ	91.09(14)
N5—Ni2—O3 ⁱⁱ	101.08(14)	N2—Ni3—N3	91.10(14)
N5 ⁱⁱ —Ni2—O3	101.08(14)	N2 ⁱ —Ni3—N3	88.91(14)
N5 ⁱⁱ —Ni2—O3 ⁱⁱ	78.92(14)	N3 ⁱ —Ni3—N3	180.0
N5—Ni2—O3	78.92(14)	O5—Ni4—N4	91.22(15)
N5 ⁱⁱ —Ni2—N8 ⁱⁱ	93.00(15)	O6—Ni4—O5	179.04(13)
N5 ⁱⁱ —Ni2—N8	87.00(15)	O6—Ni4—N1	94.61(15)
N5—Ni2—N8 ⁱⁱ	87.00(15)	O6—Ni4—N4	89.74(15)
N5—Ni2—N8	93.00(16)	N1—Ni4—O5	84.43(14)
N5—Ni2—N5 ⁱⁱ	180.0	N1—Ni4—N4	175.53(16)

Symmetry code: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y, -z+1$.

Table S5. Selected bond lengths(Å)and angles (°) parameters for **5**.

Selected bond lengths			
Ni2—O2	2.117(3)	Ni2—N2	1.959(3)
Ni2—O3	2.117(3)	Ni1—O1 ⁱ	1.853(3)
Ni2—O5	2.002(3)	Ni1—O1	1.853(3)
Ni2—O4	2.138(3)	Ni1—N1 ⁱ	1.852(3)
Ni2—N00A	1.981(3)	Ni1—N1	1.852(3)
Selected bond angle			
O2—Ni2—O3	86.71(11)	N2—Ni2—O2	78.82(12)
O2—Ni2—O4	91.63(11)	N2—Ni2—O3	97.23(12)
O3—Ni2—O4	156.69(11)	N2—Ni2—O5	89.32(13)
O5—Ni2—O2	168.14(11)	N2—Ni2—O4	105.27(12)
O5—Ni2—O3	94.56(12)	N2—Ni2—N00A	173.19(14)
O5—Ni2—O4	91.80(12)	O1—Ni1—O1 ⁱ	180.0
N00A—Ni2—O2	95.53(12)	N1—Ni1—O1	84.49(13)
N00A—Ni2—O3	78.52(12)	N1 ⁱ —Ni1—O1 ⁱ	84.49(13)
N00A—Ni2—O5	96.28(12)	N1 ⁱ —Ni1—O1	95.51(13)
N00A—Ni2—O4	78.50(12)	N1—Ni1—O1 ⁱ	95.51(13)
N1—Ni1—N1 ⁱ	180.00(14)		

Table S6. The continuous shape measures value calculated using SHAPE 2.0.

Complex	SP-4 (D_{4h} , Square)	OC-6 (O_h , Octahedron)
1A–Ni1	0.138	--
1A–Ni2	--	0.709
1A–Ni3	0.205	--
1B–Ni4	--	0.662
1B–Ni5	0.144	--
2A–Ni1	0.226	--
2A–Ni2	--	0.593
2B–Ni3	0.228	--
2B–Ni4	--	0.646
3A–Ni1	0.234	--
3A–Ni2	--	0.645
3B–Ni3	0.133	--
3B–Ni4	--	0.585
4A–Ni1	0.202	--
4A–Ni2	--	0.695
4B–Ni3	--	0.614
4B–Ni4	0.131	--
5–Ni1	0.231	--
5–Ni2	--	1.841

Table S7. Non-bonding interactions geometry (Å, °)

Complex	D—H...A	d(D—H)	d(H...A)	d(D...A)	∠DHA
1	C ₄₀ —H ₄₀ ...N ₇	0.950	2.703	3.583	154.3
	C ₁₇ —H ₁₇ ...N ₁₀	0.950	2.600	3.515	161.8
	C ₂₀ —H ₂₀ ...C ₂₄	0.950	2.851	3.633	140.3
	C ₇ —H ₇ ...C ₂₃	0.950	2.900	3.719	145.1
2	C ₂₂ —H ₂₂ ...N ₂	0.950	2.630	3.509	154.0
	C ₁₆ —H ₁₆ ...N ₇	0.950	2.614	3.549	168.2
	C ₁₁ —H ₁₁ ...N ₅	0.950	2.741	3.484	135.6
	C ₄ —H _{4B} ...C ₄₃	0.980	2.791	3.296	112.73
3	C ₂₄ —H ₂₄ ...N ₃	0.950	2.583	3.501	162.6
	C ₁₉ —H ₁₉ ...N ₆	0.950	2.723	3.617	157.2
	C ₃₉ —H ₃₉ ...O ₂	0.950	2.584	3.522	169.53
4	C ₄₅ —H ₄₅ ...N ₆	0.950	2.652	3.567	161.8
	C ₂₇ —H ₂₇ ...O ₂	0.950	2.490	3.397	159.7
5	O ₃ —H ₃ ...O ₆	0.883	1.743	2.597	162.2
	O ₆ —H _{6A} ...O ₅	0.840	1.799	2.631	170.6
	O ₇ —H ₇ ...O ₂	0.840	1.862	2.673	162.0
	O ₈ —H ₈ ...O ₇	0.870	1.899	2.753	171.6
	O ₄ —H ₄ ...O ₈	0.885	1.816	2.692	170.0

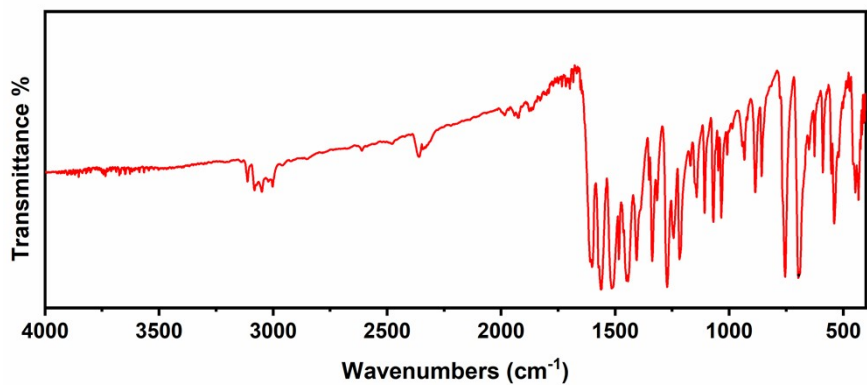


Fig. S1. The IR spectra of **1**.

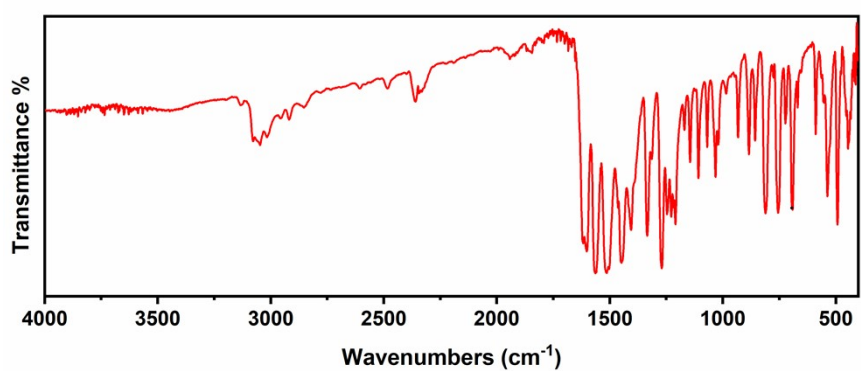


Fig. S2. The IR spectra of **2**.

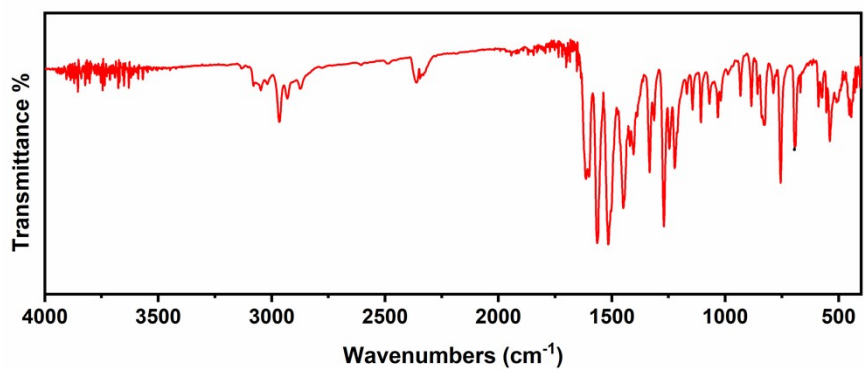


Fig. S3. The IR spectra of **3**.

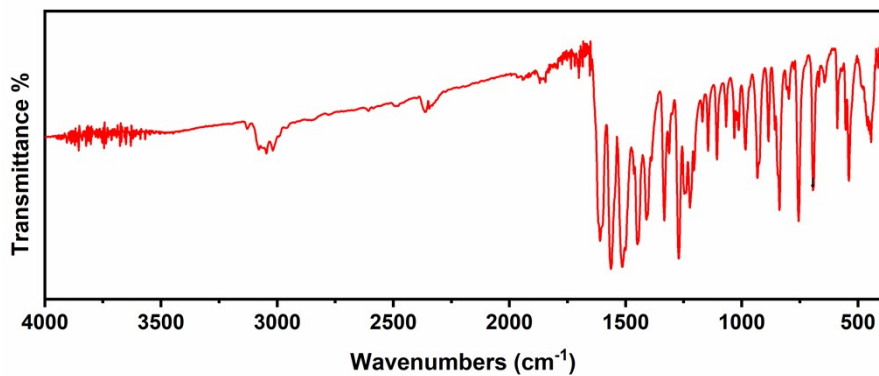


Fig. S4. The IR spectra of **4**.

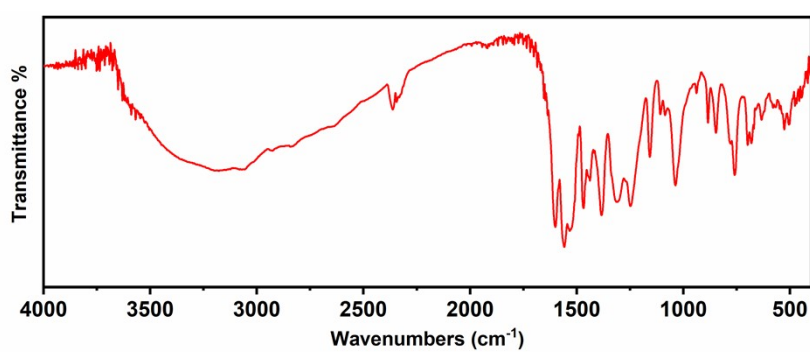


Fig. S5. The IR spectra of **5**.

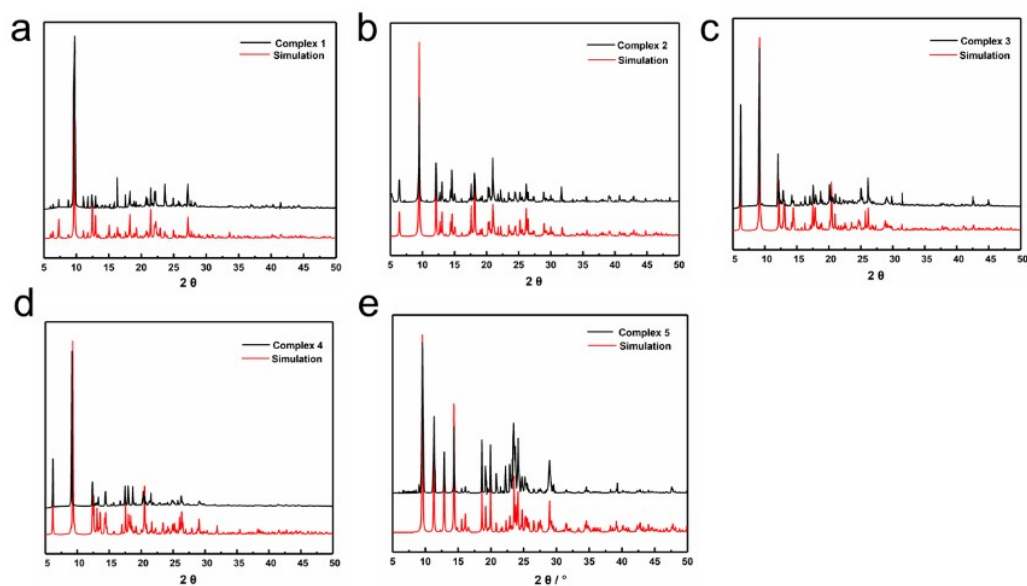


Fig. S6. PXRD patterns of **1** (a), **2** (b), **3** (c), **4** (d) and **5** (e).

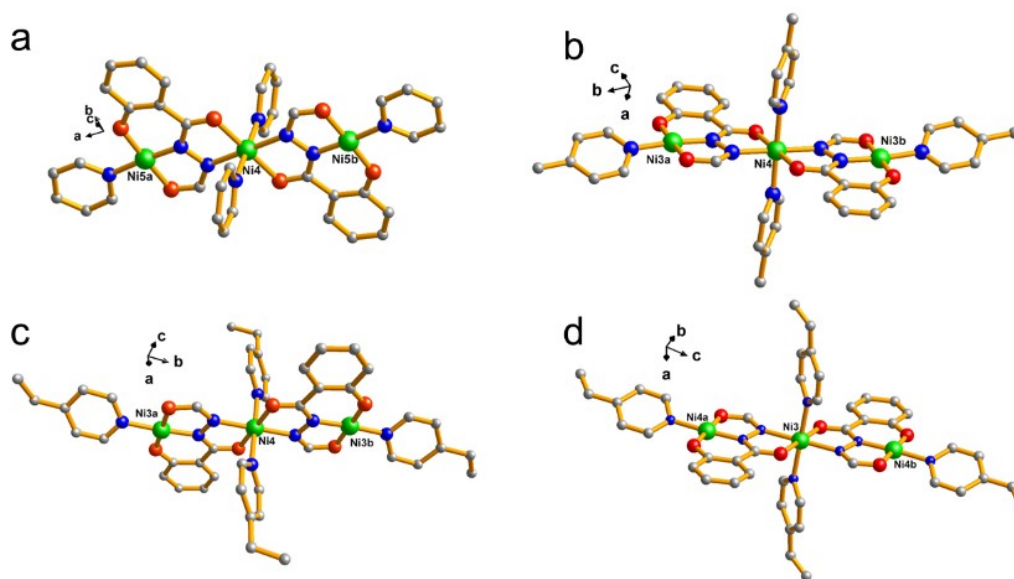


Fig. S7. Coordination environment of Ni(II) ions in **1B** (a), **2B** (b), **3B** (c) and **4B** (d). Hydrogen atoms, counter anions and free solvent molecules were omitted for clarity.

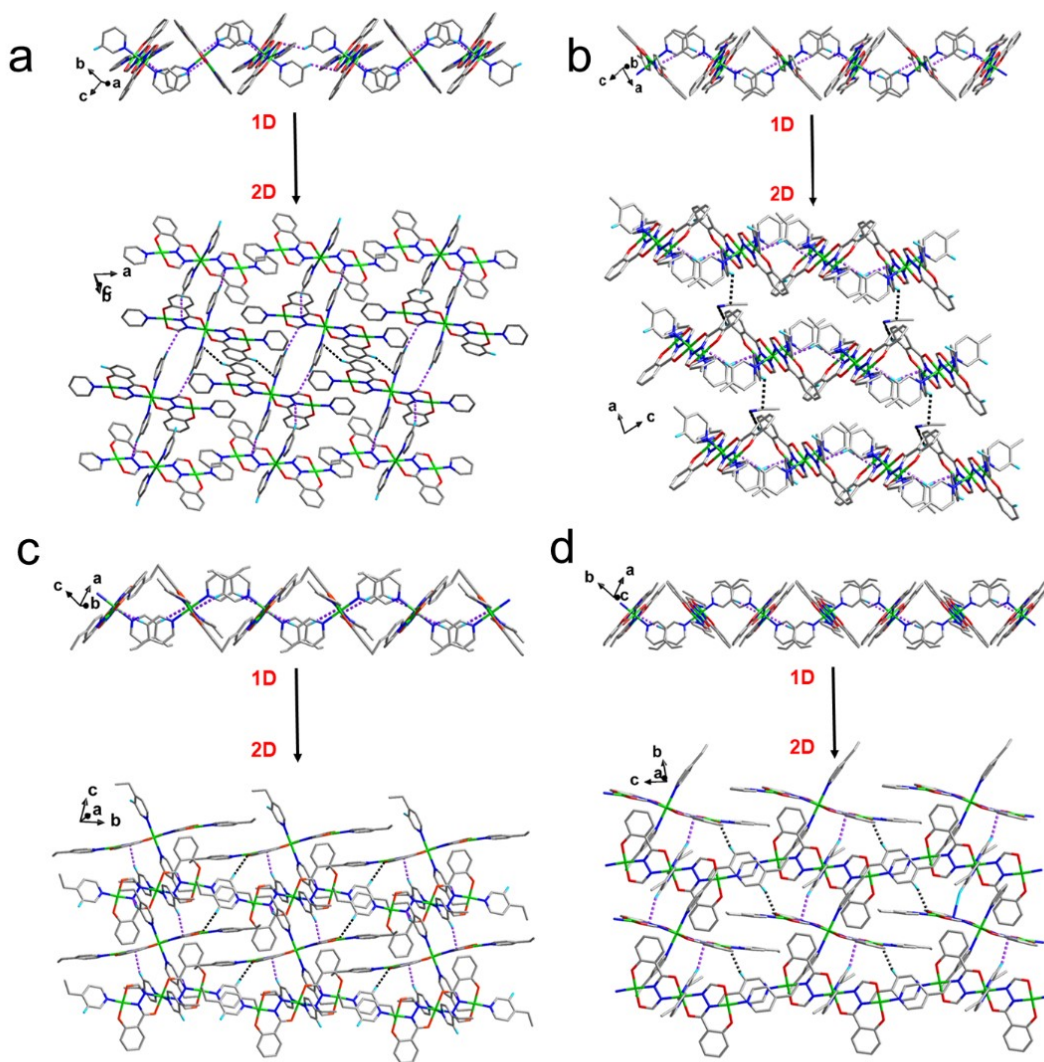


Fig. S8. The 1D chain and 2D layer of 1(a), 2(b), 3(c) and 4(d) viewed along an axis.

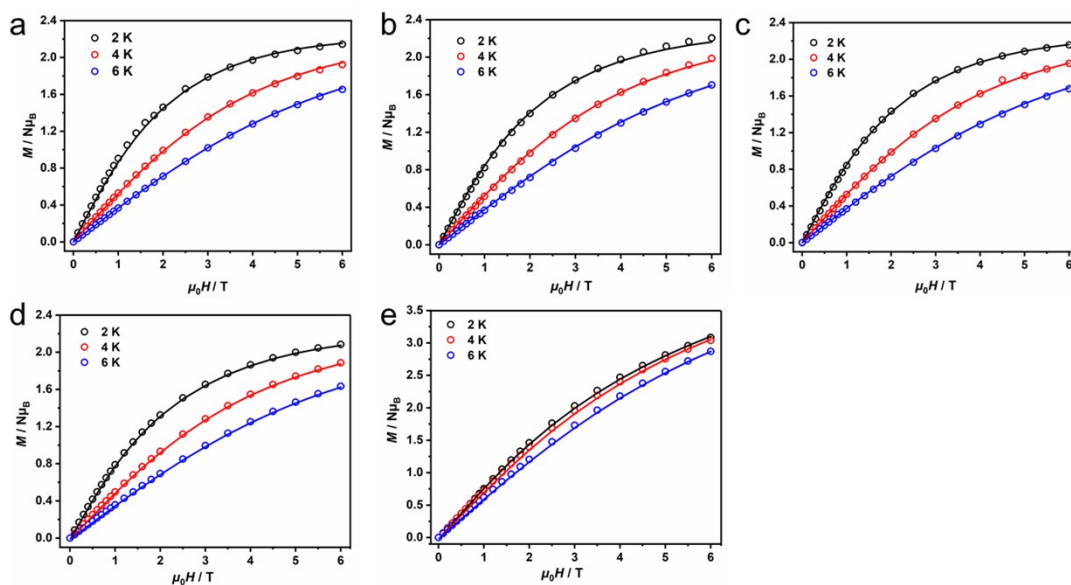


Fig. S9. Field-dependent magnetization at variable temperatures; (\circ) represents experimental data. Solid line represents the best fit of the $\chi_M T$ data by using the PHI program.

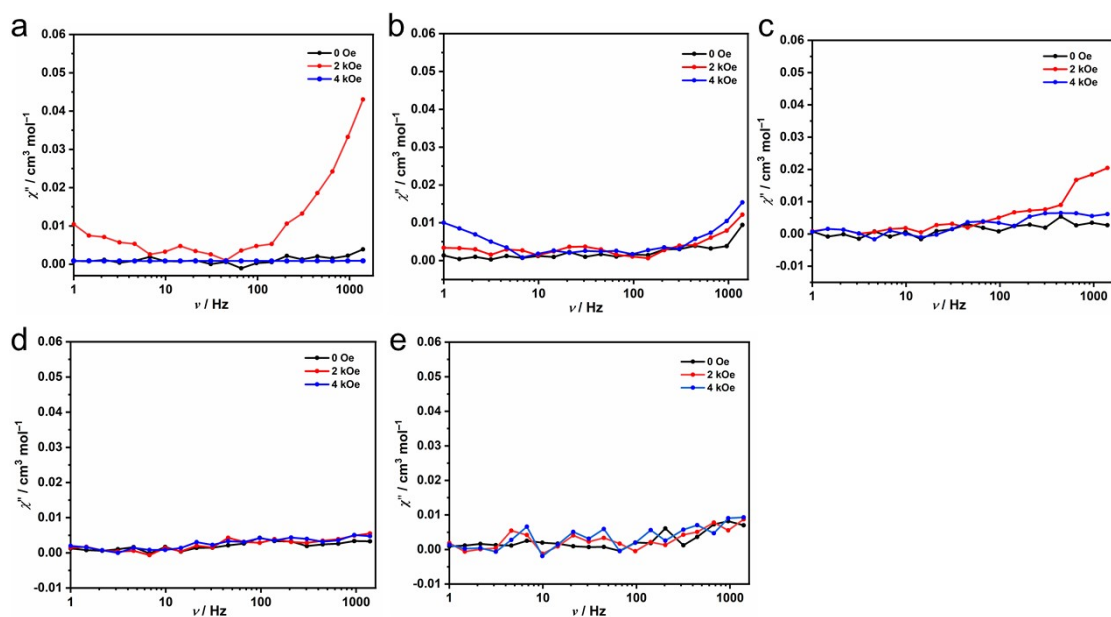


Fig. S10. Frequency dependence of the out-of-phase (χ'') ac susceptibilities measured under zero dc field at 2 K for **1** (a), **2** (b), **3** (c), **4** (d) and **5** (e).