Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

Structures and magnetism of $\{Ni_2Na_2\}$, $\{Ni_4\}$ and $\{Ni_6^{II}Ni^{III}\}$ 2-Hydroxy-3-alkoxy-benzaldehyde clusters

Shu-Hua Zhang,[a]* Ning Li[a], Cheng-Min Ge[a], Chao Feng[a], Lu-Fang Ma[b,]*

[a] *College of Chemistry and Bioengineering, Guilin University of Technology (Key Laboratory of Nonferrous and Materials Processing Technology, Ministry of Education of China), Guilin 541004, PR China*
[b] *College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, China*

Table S1. Selected bond lengths [Å] and angles [°] for **1**

NI1–O4	2.000(2)	O5– NI1–N1^{i}	172.25(11)
NI1–O1	2.011(2)	O4– NI1–N1	96.38(10)
NI1–O5	2.031(3)	O1– NI1–N1	89.56(11)
NI1–O3	2.062(3)	O5– NI1–N1	93.64(12)
NI1–N1^{i}	2.092(3)	O3– NI1–N1	174.02(12)
NI1–N1	2.112(3)	N1^{i}– NI1–N1	79.37(14)
NI1–NI1^{i}	3.235(2)	O4^{i}–Na1–O1	97.84(11)
NI1–Na1^{i}	3.485(2)	O4^{i}–Na1–O7	121.46(12)
Na1–O4^{i}	2.268(3)	O1–Na1–O7	133.91(12)
Na1–O1	2.292(3)	O4^{i}–Na1–O2	134.33(11)
Na1–O7	2.325 (4)	O1–Na1–O2	66.46(10)
Na1–O2	2.454(3)	O7–Na1–O2	96.14(12)
Na1–O6^{i}	2.527(3)	O4^{i}–Na1–O6^{i}	65.94(10)
Na1–N1^{i}	2.670(3)	O1–Na1–O6^{i}	135.49(11)
NI1^{i}–N1–NI1	100.63(14)	O7–Na1–O6^{i}	85.88(12)
O4–NI1–O1	173.78(9)	O2–Na1–O6^{i}	94.78(10)
O4–NI1–O5	89.86(11)	O4^{i}–Na1–N1	32.79(6)
O1–NI1–O5	87.93(11)	O1–Na1–N1	82.18(7)
O4–NI1–O3	87.23(11)	O2–Na1–N1	117.40(10)
O1– NI1–O3	87.01(10)	O7–Na1–N1	144.99(19)
O5– NI1–O3	91.13(11)	O6–Na1–N1	97.21(8)
O4– NI1–N1^{i}	87.60(11)	N3–N2–N1	179.7(5)
O1– M1–N1^{i}	95.32(11)		

Symmetry codes: (i) (i) $-x+1, -y+1, -z+2$.

Table S2. Selected bond lengths [Å] and angles [°] for **2.**

Ni1–O2	2.022(6)	O1^{ii}–Ni1–O4	93.0(2)
Ni1–O1	2.013(5)	O2^{ii}–Ni1–O4	98.0(2)
Ni1–O4^{i}	2.052(5)	O4^{ii}–Ni1–O4	80.5(3)
Ni1–O4^{ii}	2.061(5)	O4^{i}–Ni1–O4^{ii}	82.8(2)
Ni1–O4	2.045(5)	O1–Ni1–O5	94.8(2)

Ni1–O5	2.107(12)	O2–Ni1–O5	88.9(2)
Ni1–O5'	2.18(4)	O4–Ni1–O5^{i}	91.2(2)
Ni···Ni	3.052-3.127	O4^{i}–Ni1–O5	89.9(2)
O1–Ni1–O2	90.6(2)	O4^{ii}–Ni1–O5	169.5(2)
O1–Ni1–O4	172.6(2)	O4^{i}–Ni1–O4	83.3(2)
O2–Ni1–O4	93.8(2)	Ni1–O4–Ni1^{iii}	96.5(2)
O1^{i}–Ni1–O4	92.4(2)	Ni1^{ii}–O4–Ni1	96.5(2)
O2^{i}–Ni1–O4	176.9(2)	*Ni1^{iii}–O4–Ni1^{ii}*	*95.9(2)*

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

Table S3. Selected bond lengths [Å] and angles [°] for **3.**

Ni1−O10	1.997(4)	O4^{a}−Ni2−O2	101.8(2)
Ni1−O10^{a}	1.997(4)	O6^{a}−Ni2−O2	95.2(3)
Ni1−O12^{a}	2.005(4)	O10−Ni2−O2	153.3(2)
Ni1−O12	2.005(4)	O12^{a}−Ni2−O2	95.9(2)
Ni1−O11^{a}	2.018(4)	O1−Ni2−O2	75.6(2)
Ni1−O11	2.018(4)	O1−Ni3−O7	176.7(2)
Ni2−O1	1.965(5)	O1−Ni3−O3	87.9(3)
Ni2−O4^{a}	1.970(5)	O7−Ni3−O3	94.2(3)
Ni2−O6^{a}	2.039(6)	O1−Ni3−O11	101.6(2)
Ni2−O10	2.078(5)	O7−Ni3−O11	80.5(2)
Ni2−O12^{a}	2.093(5)	O3−Ni3−O11	99.9(2)
Ni2−O2	2.183(6)	O1−Ni3−O10	78.7(2)
Ni3−O1	1.938(5)	O7−Ni3−O10	99.3(2)
Ni3−O7	1.957(5)	O3−Ni3−O10	166.1(3)
Ni3−O3	2.073(7)	O11−Ni3−O10	79.3(2)
Ni3−O11	2.084(4)	O1−Ni3−O8	100.9(2)
Ni3−O10	2.105(5)	O7−Ni3−O8	76.4(2)
Ni3−O8	2.181(5)	O3−Ni3−O8	92.6(3)
Ni4−O7	1.959(5)	O11−Ni3−O8	154.5(2)
Ni4−O4	1.979(5)	O10−Ni3−O8	93.7(2)
Ni4−O9	2.037(6)	O7−Ni4−O4	174.7(2)
Ni4−O12	2.080(4)	O7−Ni4−O9	88.3(2)
Ni4−O11	2.119(5)	O4−Ni4−O9	94.4(2)
Ni4−O5	2.151(5)	O7−Ni4−O12	103.8(2)
Ni1···Ni2	3.093(1)	O4−Ni4−O12	80.4(2)
Ni1···Ni3	3.111(1)	O9−Ni4−O12	97.0(2)

Ni1···Ni4	3.106(1)	O7−Ni4−O11	79.5(2)
Ni2···Ni3	3.114(1)	O4−Ni4−O11	98.3(2)
Ni2···Ni4[a]	3.098(1)	O9−Ni4−O11	166.2(2)
Ni3···Ni4	3.103(2)	O12−Ni4−O11	79.8(2)
O10−Ni1−O12[a]	83.6(2)	O7−Ni4−O5	99.2(2)
O10−Ni1−O12	96.4(2)	O4−Ni4−O5	76.1(2)
O10−Ni1−O11[a]	96.0(2)	O9−Ni4−O5	96.2(2)
O10[i]−Ni1−O11[a]	84.0(2)	O12−Ni4−O5	153.8(2)
O12[a]−Ni1−O11[a]	83.7(2)	O11−Ni4−O5	92.2(2)
O12−Ni1−O11[a]	96.3(2)	Ni3−O1−Ni2	105.8(2)
O1−Ni2−O4[a]	176.7(2)	Ni4−O7−Ni3	104.4(2)
O1−Ni2−O6[a]	95.0(2)	Ni1−O10−Ni2	98.8(2)
O4[a]−Ni2−O6[a]	87.2(2)	Ni1−O10−Ni3	98.5(2)
O1−Ni2−O10	79.0(2)	Ni2−O10−Ni3	96.3(2)
O4[a]−Ni2−O10	103.3(2)	Ni1−O11−Ni3	98.7(2)
O6[a]−Ni2−O10	95.0(2)	Ni1−O11−Ni4	97.2(2)
O1−Ni2−O12[a]	98.1(2)	Ni3−O11−Ni4	95.1(2)
O4[a]−Ni2−O12[a]	80.0(2)	Ni1−O12−Ni4	98.9(2)
O6[a]−Ni2−O12[a]	164.6(2)	Ni1−O12−Ni2[a]	97.8(2)
O10−Ni2−O12[a]	79.7(2)	Ni4−O12−Ni2[a]	95.9(2)

Symmetry codes: (a) − x + 1/2, − y + 3/2, − z.

Table S4 Coordination number (*N*), bond valence sum (*BVS*), expected atomic valence (*V*) and deviation from the expected atomic valence (Δ*V*) for the nickel cations.

	Ni1	Ni2	Ni3	Ni4
N	6	6	6	6
BVS	2.98	2.07	2.06	2.07
V	+3	+2	+2	+2
ΔV	0.02	0.07	0.06	0.07

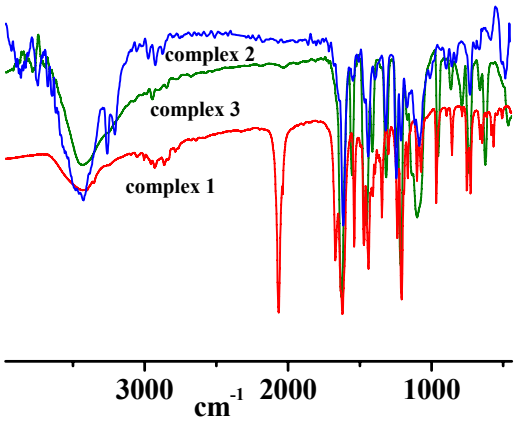
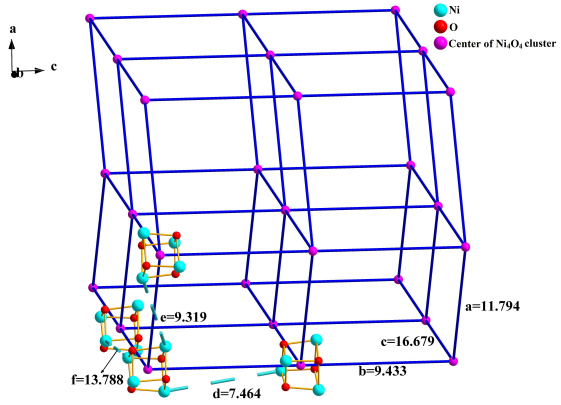


Fig. S1. IR contrast of **1-3**.



Scheme S1. Illustration of correlation representing the distance (a,b,c) between the adjacent $\{Ni_4O_4\}$ center,along a,b,c axial, (e, f, d) the M···M distances of adjacent $\{Ni_4O_4\}$ in a, b, c axial.

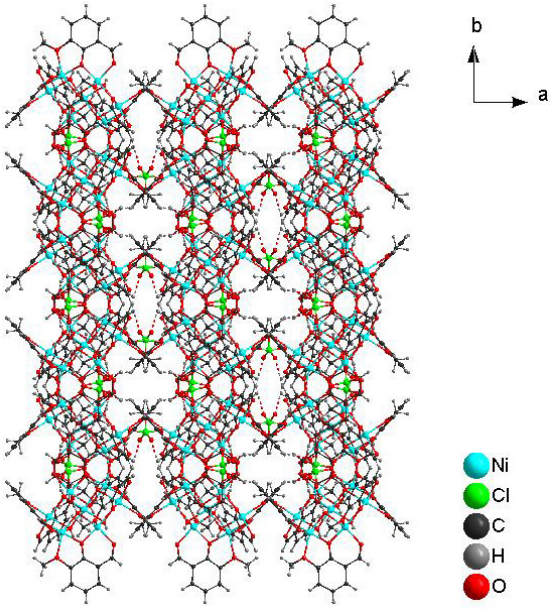


Fig. S2 Packing drawing of the **3**.

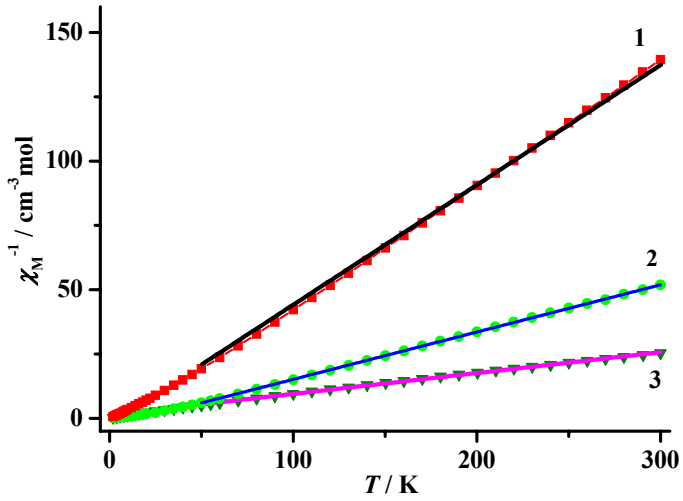


Fig. S3 Plot of χ_M^{-1} *vs T* for **1 – 3**. The solid line represents a fit of data in the temperature range 50-300 K.

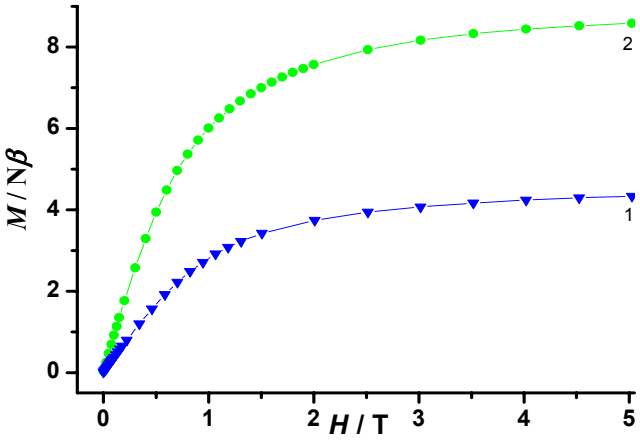


Fig. S4 Field dependence of magnetization at 2 K for **1 – 2**.

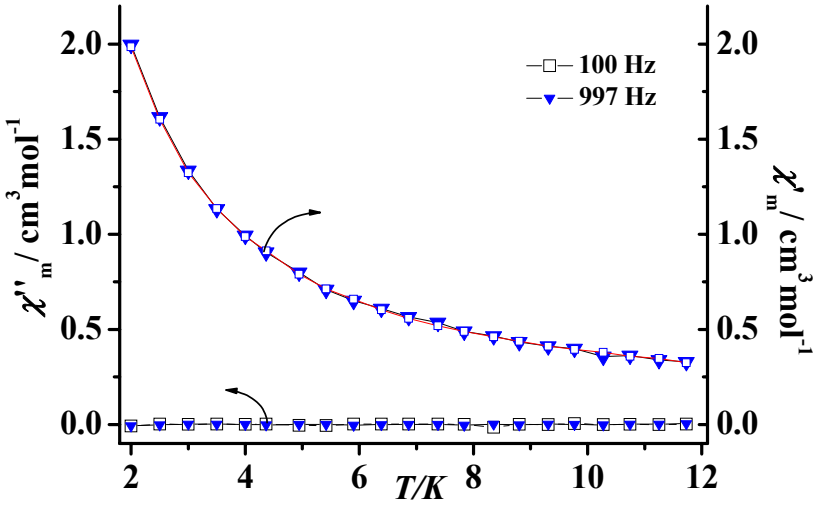


Fig. S5 In-phase and out-of-phase ac the range of 2-11.7 K for **1**.

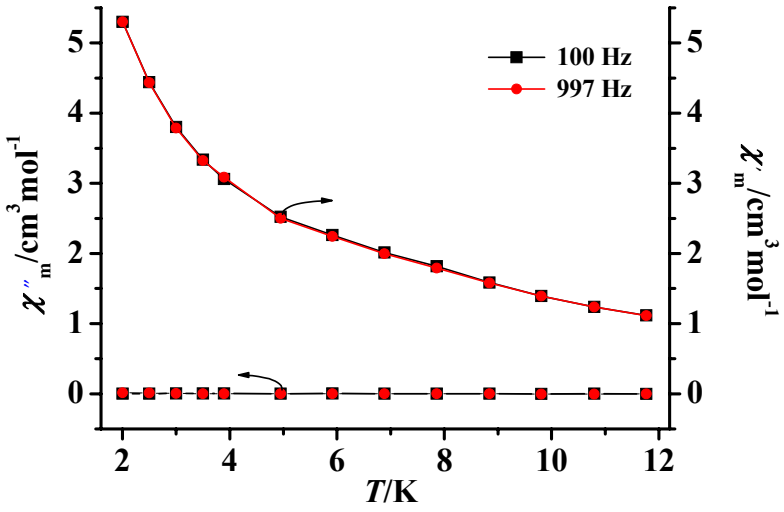


Fig. S6 In-phase and out-of-phase ac the range of 2-12 K for 2.