Ni^{II}, Mn^{II} and Co^{II} coordination polymers with 1,4-naphthalenedicarboxylic acid exhibiting metamagnetic and antiferromagnetic behaviors

Ya-Min Li,*,† Xue-Fei Li,† Ying-Ying Wu,† Daniel L. Collins-Wildman,††
Sheng-Min Hu,††† Ying Liu,† Hai-Yan Li,† Xiao-Wei Zhao,*,† Lin-Yu Jin,† and
Dong-Bin Dang*,†

†Henan Key Laboratory of Polyoxometalate, Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, PR China

††Department of Chemistry, Emory University, Atlanta, GA 30322, USA

†††State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

Supporting Information

Experimental Section

X-Ray Crystallography

Figure S1 IR spectra of compounds **1**–**3**.

Figure S2 PXRD curves of compounds **1**–**3**.

Figure S3 TG curves of compounds **1**–**3**.

Figure S4. 3D network configuration of compound **1**.

Figure S5. The coordination geometry of Mn^{II} centers showing thermal ellipsoids at 50 % probability in **2**. Symmetry codes: A: 1–*x*, 1–*y*, 2–*z*; B: 2–*x*, 1–*y*, 2–*z*; C: 1+*x*, *y*, *z*; D: 2–*x*, –0.5+*y*, 1.5–*z*; E: 1–*x*, 0.5+*y*, 1.5–*z*.

Figure S6. 3D network configuration of compound **2**.

Figure S7. The coordination geometry of trinuclear Co^{II} cluster showing thermal ellipsoids at 50% probability in **3**. Symmetry codes: A: 1–*x*, 1–*y*, 1–*z*.

Figure S8. 3D network configuration of compound **3**.

Figure S9. (a) The FCM and ZFCM curves of compound **1** at 100 Oe and 200 Oe; (b) The plots of χ' *vs. T* and the χ'' *vs. T* curves of compound **1**.

Figure S10. Two kinds of magnetic coupling exchange interactions in compound **1**.

Figure S11. (a) The χ_m^{-1} *vs. T* plots of compound **2**. (b) *M vs. H* curve of compound **2** at 2 K.

Figure S12. The *M vs. H* curve of compound **3** at 2 K.

Table S1. Crystallographic Data and Refinement Details for compounds **1–3**.

Table S2 BVS analyses of compounds **1**–**3**.

Table S3 Selected bond lengths (Å) and bond angles (°) for compounds **1**–**3**.

Experiment section

Materials and Methods

All purchased reagents were used as received from the vendor without modification. Infrared spectra of KBr pellets were taken using a Bruker VERTEX-70 FT-IR spectrophotometer with an operating range of 400–4000 cm^{-1}. Elemental analyses were carried out on a via Vario EL III Etro Elemental Analyzer. Powder X-ray diffraction (PXRD) data were taken with a Bruker D8 Advance diffractometer using CuKα radiation with 2θ angles ranging from 5 to 50°. Thermogravimetric analyses (TGA) were carried out within a heating range of 30 to 1000 °C with a NETZSCH STA449F5 instrument under flowing N_2 while increasing temperature by 20 ºC/min. A Quantum Design MPMS-XL SQUID magnetometer was used for the magnetic measurements.

Synthesis of $[Ni_4(1,4\text{-ndc})_3(OH)_2(H_2O)_2{\cdot}2.5H_2O]_n$ (1)

In a stainless steel bomb lined with Teflon, $Ni(OAc)_2{\cdot}4H_2O$ (0.5 mmol, 0.372 g), 1,4-H_2ndc (0.4 mmol, 0.086 g), 2,4-diamino-6-methyl-1,3,5-triazine (0.1 mmol, 0.012 g) and H_2O (6 mL) were stirred for 40 min. This solution was heated at 160 ºC for 3 days, followed by cooling to room temperature. Green block crystals of **1** were collected and washed with H_2O (yield: 0.065 g, 52.4 % based on $Ni(OAc)_2{\cdot}4H_2O$). Elemental analysis (%): calcd for C 43.57, H 2.95. Found C 43.52, H 3.03. IR (KBr, cm^{-1}): 3433 m, 1606 s,1541 m, 1512 w, 1461 w, 1414 s, 1371m, 1333 s, 1265 m, 1210 w, 1158 w, 827 m, 785 m.

Synthesis of $\{[Mn_2(1,4\text{-ndc})_2(OAc)](C_5MIm){\cdot}0.5H_2O\}_n$ (2)

In a stainless steel bomb lined with Teflon, $Mn(OAc)_2{\cdot}4H_2O$ (1.5 mmol, 0.368 g), 1,4-H_2ndc (0.5 mmol, 0.108 g), and triethylamine (3 mL) were stirred for 20 min followed by the addition of $[C_5MIm]Br$ (4.3 mmol, 1 g), then stirred for another 20 min. This solution was heated at 160 ºC for 5 days, followed by cooling to room temperature. Yellow block crystals of **2** were collected and washed with triethylamine (yield: 0.112 g, 58.99 % based on 1,4-ndc^{2-}). Elemental analysis (%): calcd for C 55.35, H 4.38, N 3.69 Found C 55.31, H 4.43, N 3.71. IR (KBr, cm^{-1}): 3424 m, 3097 m, 2924 m, 1568 s, 1467 m, 1407 s, 1367 s, 1263 m, 1166 m, 1027w, 791 m, 673 m, 807 m, 622 m, 547 m.

Synthesis of $\{[Co_3(1,4\text{-ndc})_4(H_2O)_4](C_5MIm)_2{\cdot}2H_2O\}_n$ (3)

In a stainless steel bomb lined with Teflon, $Co(OAc)_2{\cdot}4H_2O$ (1.5 mmol, 0.375 g,), 1,4-H_2ndc (0.5 mmol, 0.108 g), $[C_5MIm]Br$ (4.3 mmol, 1 g) and NaOH (12.5 mmol/L, 5 mL) were stirred for 40 min. This solution was heated at 160 ºC for 5 days, followed by cooling to room temperature. The resulting solution was filtered and left at room temperature to evaporate for 3 weeks. Red block crystals of **3** were collected and washed with H_2O (yield: 0.121 g, 66.85 % based on 1,4-ndc^{2-}). Elemental analysis (%): calcd for C 54.74, H 4.87, N 3.87. Found C 54.78, H 4.89, N 3.82 IR (KBr, cm^{-1}): 3416 m, 2933 w, 2870 w, 1616 s,1414 s, 1368 s, 1254 m, 1210 w, 1163 m, 869 w, 792 m, 586 w.

Crystallographical Section

Single crystal X-ray diffraction data were collected on a Bruker Apex-II using a CCD area-detector and MoKα radiation (λ = 0.71073 Å) at 296(2) K for compounds **1** and **3** and an Agilent SuperNova diffractometer using CuKα radiation (λ = 1.54184 Å) at 293(2) K for compound **2**. The reductions of data and corrections to absorption values were done via empirical methods. SHELXS-97[1] was used to solve the structure with direct methods, and this data was further refined with the full matrix least-squares method in SHELXL-97.[2] All atoms were refined anisotropically other than hydrogen

atoms whose positions on the ligands were calculate and subsequently refined with a riding model while the hydrogen atoms of the hydroxyl groups and some water molecules were found by difference Fourier maps. The crystal parameters, data collection, and details of refinement for compounds **1**–**3** are listed in Table S1. Various bond angles and lengths of compounds **1**–**3** are summarized in Table S3.

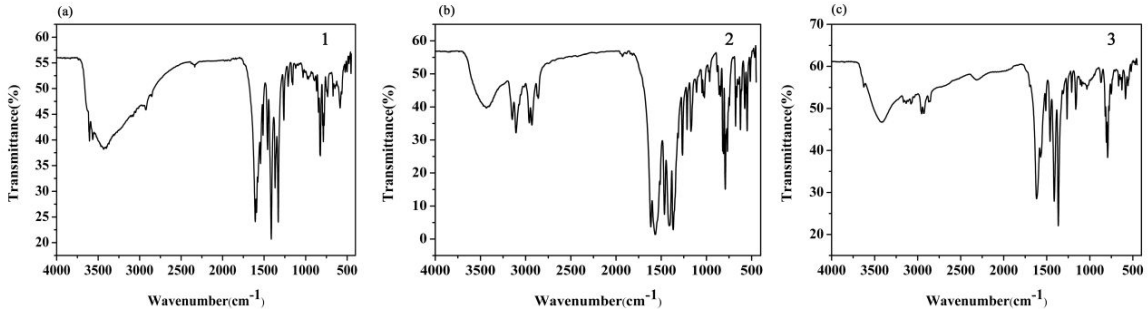

Figure S1. IR spectra of compounds **1**–**3**.

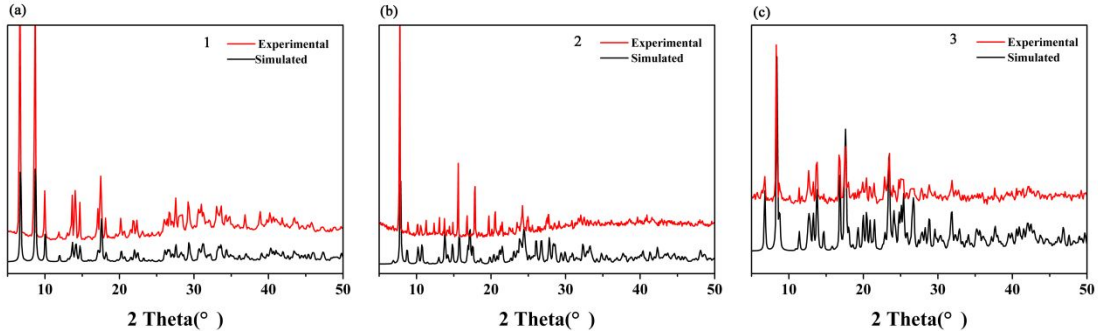

Figure S2. PXRD curves of compounds **1**–**3**.

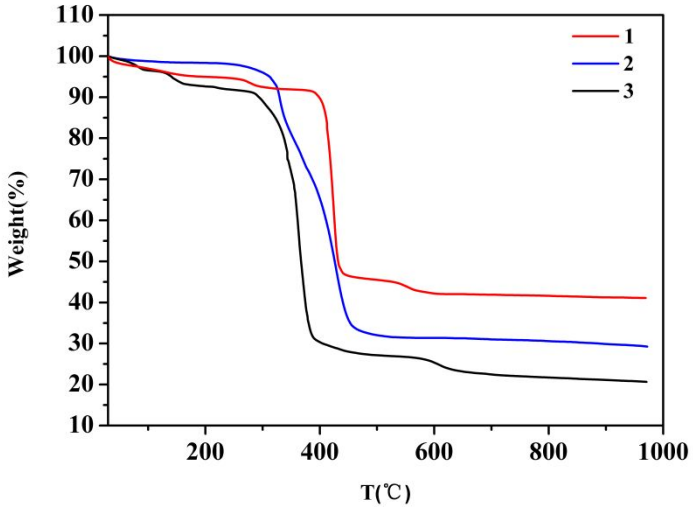

Figure S3. TG curves of compounds **1**–**3**.

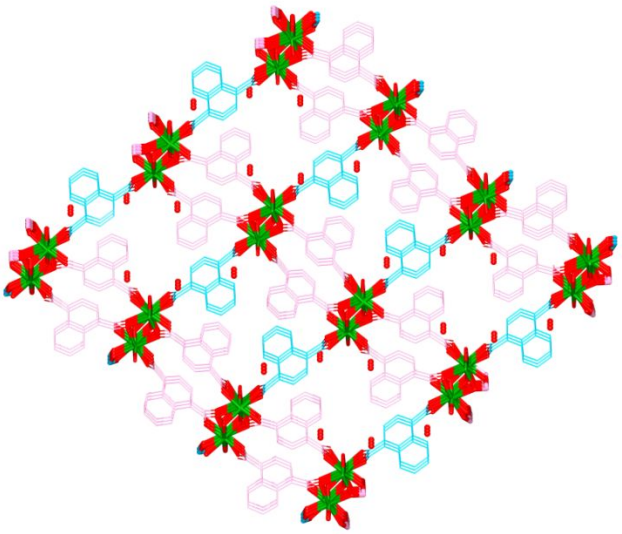

Figure S4. 3D network configuration of compound **1**. Color scheme: Ni green, O red, C rose and sky blue.

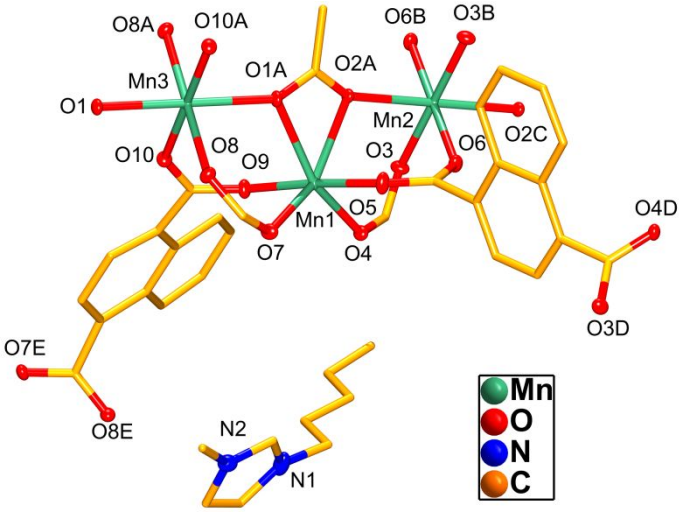

Figure S5. The coordination geometry of Mn^{II} centers showing thermal ellipsoids at 50 % probability in **2**. Symmetry codes: A: 1–*x*, 1–*y*, 2–*z*; B: 2–*x*, 1–*y*, 2–*z*; C: 1+*x*, *y*, *z*; D: 2–*x*, –0.5+*y*, 1.5–*z*; E: 1–*x*, 0.5+*y*, 1.5–*z*.

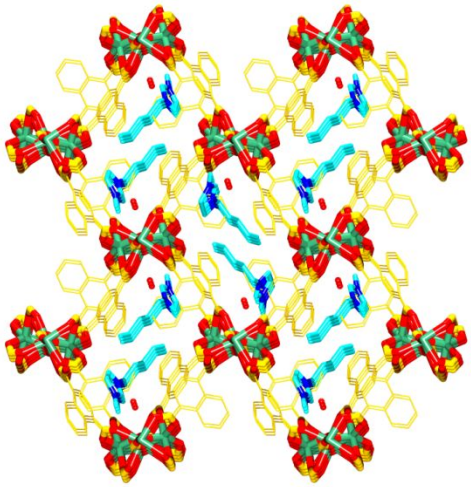

Figure S6. 3D network configuration of compound **2**. Color scheme: Mn sea green, O red, N blue, C gold and turquiose.

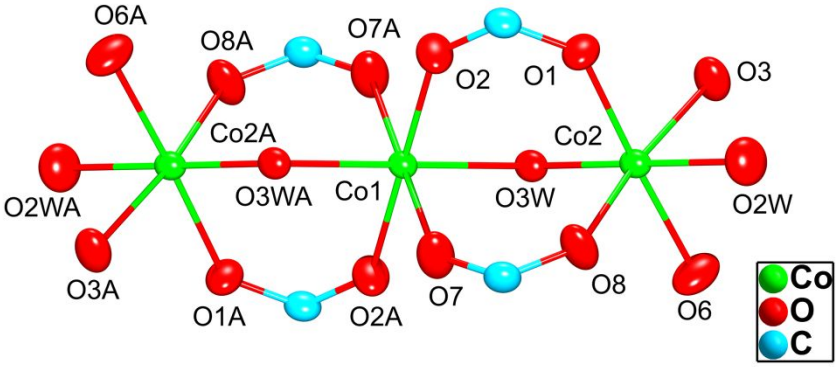

Figure S7. The coordination geometry of trinuclear Co^{II} cluster showing thermal ellipsoids at 50% probability in **3**. Symmetry codes: A: 1–*x*, 1–*y*, 1–*z*.

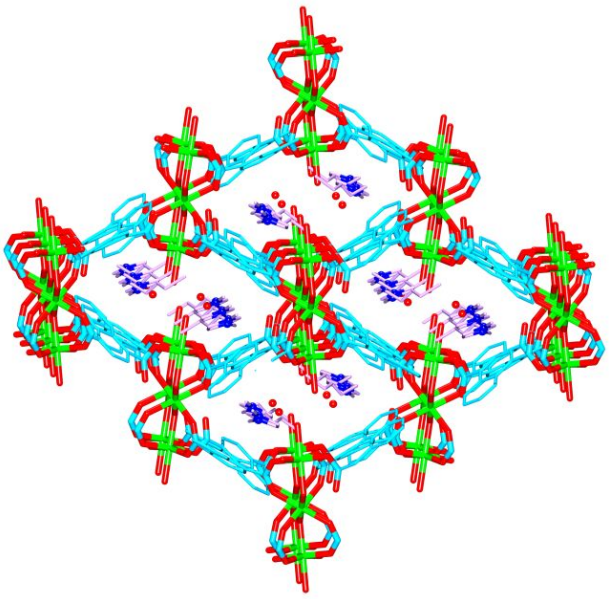

Figure S8. 3D network configuration of compound **3**. Color scheme: Co bright green, O red, N plum, C sky blue and lavender.

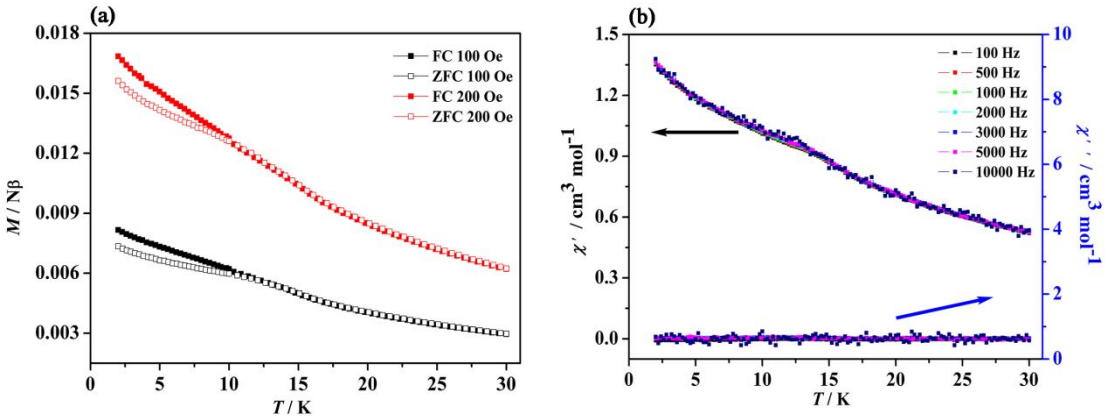

Figure S9. (a) The FCM and ZFCM curves of compound **1** at 100 Oe and 200 Oe; (b) The plots of χ' *vs. T* and the χ'' *vs. T* curves of compound **1**.

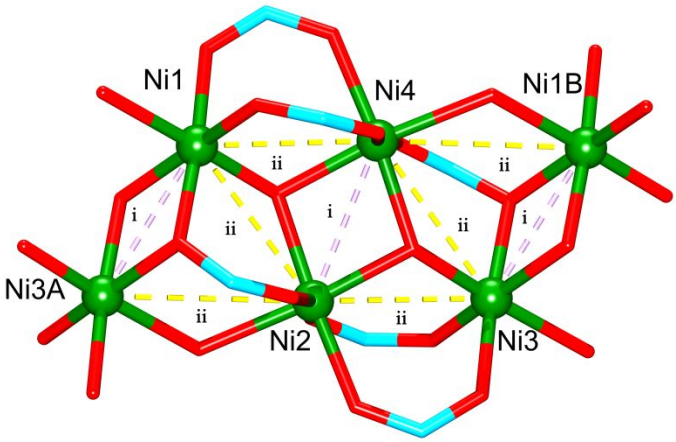

Figure S10. Two kinds of magnetic coupling exchange interactions in compound **1**.

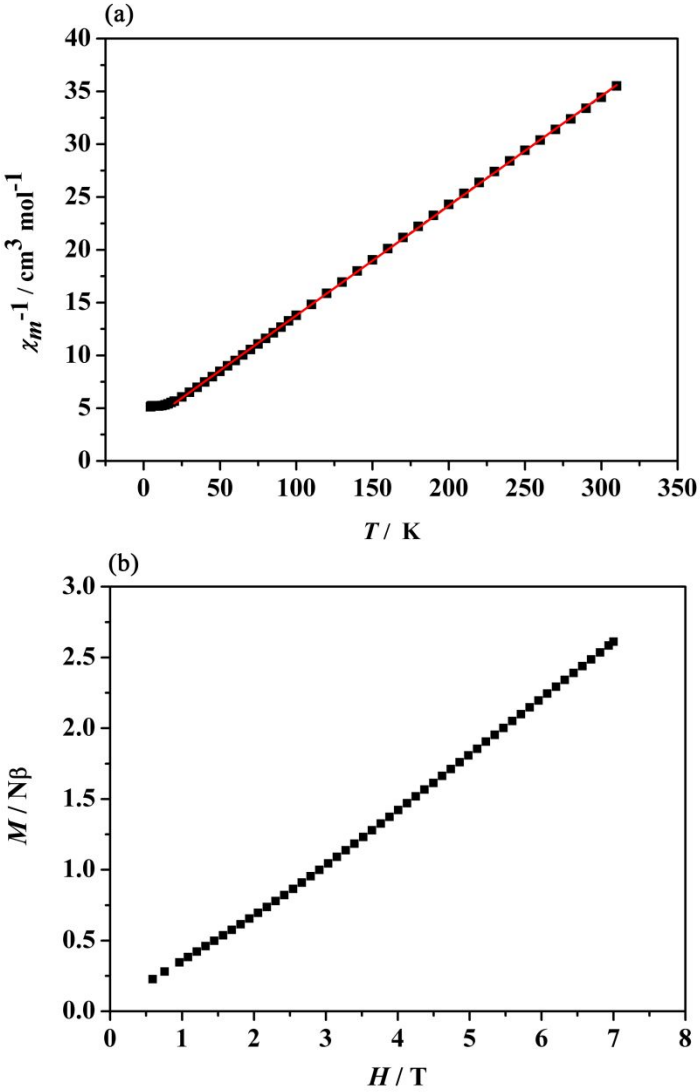

Figure S11. (a) The χ_m^{-1} *vs. T* plots of compound **2**. (b) *M vs. H* curve of compound **2** at 2 K.

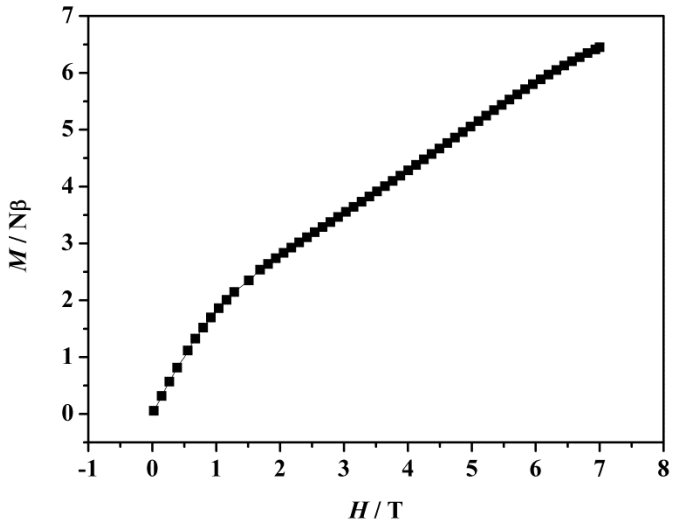

Figure S12. The *M vs. H* curve of compound **3** at 2 K.

Table S1. Crystallographic Data and Refinement Details for compounds **1–3**.

	1	**2**	**3**
Empirical formula	$C_{36}H_{29}Ni_4O_{18.5}$	$C_{35}H_{33}Mn_2N_2O_{10.5}$	$C_{66}H_{70}Co_3N_4O_{22}$
Formula weight	992.43	759.51	1448.05
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$
a (Å)	7.0774(8)	12.8396(11)	14.641(2)
b (Å)	13.6205(14)	16.4520(18)	16.195(2)
c (Å)	20.681(2)	15.4674(2)	15.584(2)
α (°)	98.818(2)		
β (°)	95.963(2)	93.7782(10)	117.203(2)
γ (°)	101.624(2)		
V (Å^3)	1910.9(4)	3260.21(6)	3286.5(8)
Z	2	4	2
T (K)	296(2)	293(2)	296(2)
D_c (g cm^{-3})	1.725	1.547	1.463
μ (mm^{-1})	2.021	6.859	0.829
F(000)	1010	1564	1502
R_{int}	0.0192	0.0252	0.0485
Ref. collected	6694	6410	7861
Ref. unique	5461	5776	5663
R index [$I>2\sigma(I)$]	R_1=0.0332, wR_2=0.1024	R_1=0.0367, wR_2=0.0920	R_1=0.0534, wR_2=0.1423

R(all data)	R_1=0.0451, wR_2=0.1190	R_1=0.0422 wR$_2$=0.0957	R_1=0.0796, wR_2=0.1625
GOOF	1.115	1.042	1.022
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (eÅ^{-3})	0.602/–0.649	1.230/–0.566	0.982/–0.787

$R = \sum(||F_o|-|F_c||)/\sum|F_o|$, $wR = \{\sum w[(F_o^2-F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, $P = (F_o^2+2F_c^2)/3]$. **1**: a = 0.0718, b = 0.0000; **2**: a = 0.0476, b = 3.6009; **3**: a = 0.0938, b = 1.3498.

Table S2. BVS analyses of compounds **1**–**3**.

compound **1**						
Atoms	Ni1	Ni2	Ni3	Ni4	μ_3-O3	μ_3-O4
BVS	1.99	2.00	2.02	1.99	1.17	1.14
Assignment	Ni^{2+}	Ni^{2+}	Ni^{2+}	Ni^{2+}	OH^{-}	OH^{-}
compound **2**				compound **3**		
Atoms	Mn1	Mn2	Mn3	Co1	Co2	
BVS	2.07	2.23	2.05	2.10	2.01	
Assignment	Mn^{2+}	Mn^{2+}	Mn^{2+}	Co^{2+}	Co^{2+}	

The oxidation state of a particular atom can be taken as the nearest integer to the value.

Table S3. Selected bond lengths (Å) and bond angles (°) of compounds **1–3**.

Compound **1**			
Bond length (Å)			
Ni1–O4	1.988(2)	Ni1–O8	2.010(2)
Ni1–O12	2.036(2)	Ni1–O14	2.095(2)
Ni1–O13	2.110(2)	Ni1–O1W	2.167(2)
Ni2–O3	2.013(2)	Ni2–O4#1	2.018(2)
Ni2–O11	2.043(2)	Ni2–O10	2.056(2)
Ni2–O1	2.065(2)	Ni2–O2W#1	2.208(2)
Ni3–O3	1.974(2)	Ni3–O9	1.988(2)
Ni3–O2	2.033(2)	Ni3–O13	2.068(2)
Ni3–O14	2.136(2)	Ni3–O2W	2.189(2)
Ni4–O3	2.022(2)	Ni4–O6	2.035(2)
Ni4–O4#1	2.038(2)	Ni4–O7	2.044(2)
Ni4–O5	2.070(2)	Ni4–O1W	2.195(2)
Bond angles (°)			

O4–Ni1–O8	101.68(10)	O4–Ni1–O12	90.20(10)
O8–Ni1–O12	93.77(10)	O4–Ni1–O14	85.63(9)
O8–Ni1–O14	168.32(9)	O12–Ni1–O14	95.32(9)
O4–Ni1–O13	93.98(9)	O8–Ni1–O13	87.01(9)
O12–Ni1–O13	175.52(9)	O14–Ni1–O13	83.37(9)
O4–Ni1–O1W	173.98(10)	O8–Ni1–O1W	83.76(10)
O12–Ni1–O1W	86.86(10)	O14–Ni1–O1W	89.42(9)
O13–Ni1–O1W	88.83(9)	O3–Ni2–O4#1	81.92(10)
O3–Ni2–O11	94.46(10)	O4#1–Ni2–O11	176.26(10)
O3–Ni2–O10	91.24(10)	O4–Ni2–O10#1	92.69(10)
O11–Ni2–O10	86.41(10)	O3–Ni2–O1	101.83(10)
O4#1–Ni2–O1	89.84(10)	O11–Ni2–O1	91.84(10)
O10–Ni2–O1	166.92(10)	O3–Ni2–O2W#1	175.35(9)
O4#1–Ni2–O2W#1	93.68(9)	O11–Ni2–O2W#1	89.91(9)
O10–Ni2–O2W#1	87.46(9)	O1–Ni2–O2W#1	79.57(9)
O3–Ni3–O9	102.67(10)	O3–Ni3–O2	91.31(10)
O9–Ni3–O2	92.69(10)	O3–Ni3–O13	85.82(10)
O9–Ni3–O13	167.47(9)	O2–Ni3–O13	96.35(9)
O3–Ni3–O14	93.72(9)	O9–Ni3–O14	86.85(9)
O2–Ni3–O14	174.93(9)	O13–Ni3–O14	83.38(9)
O3–Ni3–O2W	172.91(9)	O9–Ni3–O2W	84.17(10)
O2–Ni3–O2W	86.45(9)	O13–Ni3–O2W	87.74(9)
O14–Ni3–O2W	88.48(9)	O3–Ni4–O6	86.97(10)
O3–Ni4–O4#1	81.21(10)	O6–Ni4–O4#1	100.13(10)
O3–Ni4–O7	92.13(10)	O6–Ni4–O7	169.53(10)
O4#1–Ni4–O7	90.02(10)	O3–Ni4–O5	174.51(10)
O6–Ni4–O5	95.73(10)	O4#1–Ni4–O5	93.59(9)
O7–Ni4–O5	86.06(10)	O3–Ni4–O1W	93.23(9)
O6–Ni4–O1W	82.30(9)	O4#1–Ni4–O1W	173.76(9)
O7–Ni4–O1W	87.34(10)	O5–Ni4–O1W	91.87(9)

#1: $-1+x, y, z$

Compound **2**			
Bond length (Å)			
Mn1–O4	2.1143(15)	Mn1–O7	2.1310(16)
Mn1–O9	2.1436(16)	Mn1–O5	2.1595(16)
Mn1–O2#1	2.2887(16)	Mn1–O1#1	2.3134(16)

Mn2–O3#1	2.1355(15)	Mn2–O3	2.1355(15)
Mn2–O6	2.1434(16)	Mn2–O6#1	2.1434(16)
Mn2–O2#3	2.1910(15)	Mn2–O2#1	2.1910(15)
Mn3–O1#1	2.1769(15)	Mn3–O1	2.1769(15)
Mn3–O8	2.1816(16)	Mn3–O8#1	2.1816(16)
Mn3–O10	2.2006(15)	Mn3–O10#1	2.2006(15)
Bond angles (°)			
O4–Mn1–O7	113.70(6)	O4–Mn1–O9	87.25(6)
O7–Mn1–O9	91.75(6)	O4–Mn1–O5	91.76(6)
O7–Mn1–O5	85.33(6)	O9–Mn1–O5	176.25(7)
O4–Mn1–O2#1	98.54(6)	O7–Mn1–O2#1	146.45(6)
O9–Mn1–O2#1	99.10(6)	O5–Mn1–O2#1	84.62(6)
O4–Mn1–O1#1	153.65(6)	O7–Mn1–O1#1	92.44(6)
O9–Mn1–O1#1	88.81(6)	O5–Mn1–O1#1	93.66(6)
O2#1–Mn1–O1#1	56.45(5)	O3#1–Mn2–O3	180.00(7)
O3#1–Mn2–O6#1	91.34(6)	O3–Mn2–O6#1	88.66(6)
O3#1–Mn2–O6	88.66(6)	O3–Mn2–O6	91.34(6)
O6#1–Mn2–O6	179.998(1)	O3#1–Mn2–O2#3	86.97(6)
O3–Mn2–O2#3	93.03(6)	O6#1–Mn2–O2#3	90.19(6)
O6–Mn2–O2#3	89.81(6)	O3#1–Mn2–O2#1	93.03(6)
O3–Mn2–O2#1	86.97(6)	O6#1–Mn2–O2#1	89.81(6)
O6–Mn2–O2#1	90.19(6)	O2#3–Mn2–O2#1	180.0
O1#1–Mn3–O1	180.0	O1#1–Mn3–O8	86.62(6)
O1#1–Mn3–O8#1	93.38(6)	O1–Mn3–O8	93.38(6)
O1–Mn3–O8#1	86.62(6)	O8–Mn3–O8#1	180.00(8)
O1#1–Mn3–O10	95.13(6)	O1–Mn3–O10	84.87(6)
O8–Mn3–O10	91.42(6)	O8#1–Mn3–O10	88.58(6)
O1#1–Mn3–O10#1	84.86(6)	O1–Mn3–O10#1	95.13(6)
O8–Mn3–O10#1	88.58(6)	O8#1–Mn3–O10#1	91.42(6)
O10–Mn3–O10#1	179.999(1)		

#1: 1–*x*, 1–*y*, 1–*z*; #1: 2–*x*, 1–*y*, 2–*z*; #3: 1+*x*, *y*, *z*.

Compound **3**			
Bond length (Å)			
Co1–O2	2.064(2)	Co1–O2#1	2.064(2)
Co1–O7	2.084(2)	Co1–O7#1	2.084(2)
Co1–O3W	2.096(2)	Co1–O3W#1	2.096(2)

Co2–O8	2.047(2)	Co2–O1	2.065(2)
Co2–O3	2.072(2)	Co2–O6	2.083(2)
Co2–O3W	2.160(2)	Co2–O2W	2.171(2)
Bond angles (°)			
O2#1–Co1–O2	180.00(13)	O2#1–Co1–O7	85.51(10)
O2–Co1–O7	94.49(10)	O2#1–Co1–O7#1	94.49(10)
O2–Co1–O7#1	85.51(10)	O7–Co1–O7#1	180.0
O2#1–Co1–O3W	89.56(8)	O2–Co1–O3W	90.44(8)
O7–Co1–O3W	93.46(9)	O7#1–Co1–O3W	86.54(9)
O2#1–Co1–O3W#1	90.44(8)	O2–Co1–O3W#1	89.56(8)
O7–Co1–O3W#1	86.54(9)	O7#1–Co1–O3W#1	93.46(9)
O3W–Co1–O3W#1	180.00(11)	O8–Co2–O1	92.14(10)
O8–Co2–O3	169.25(9)	O1–Co2–O3	88.21(9)
O8–Co2–O6	88.74(10)	O1–Co2–O6	177.34(9)
O3–Co2–O6	90.45(10)	O8–Co2–O3W	99.29(8)
O1–Co2–O3W	91.64(8)	O3–Co2–O3W	91.44(8)
O6–Co2–O3W	90.70(9)	O8–Co2–O2W	83.39(9)
O1–Co2–O2W	90.46(9)	O3–Co2–O2W	85.86(9)
O6–Co2–O2W	87.15(10)	O3W–Co2–O2W	176.53(8)

#1: 1–*x*, 1–*y*, 1–*z*.

References

(1) Sheldrick, G. M. SHELXS-97, *Program for X-ray Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

(2) Sheldrick, G. M. SHELXL-97, *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.