Electronic Supplementary Information

Chiral Metal−Organic Frameworks Constructed by Four-fold Helical Chain SBUs for Enantioselective Recognition α-hydroxy/amino Acids

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Section S1: Computational details

Grand canonical Monte Carlo simulations were performed to study the interaction of **1** with mandelic acid by Sorption module of Accelrys Materials Studio 61 package. Geometries of mandelic acid were optimized by density-functional theory in DMol3. The Lennard–Jones potential were evaluated by the atom-based method with a spherical cutoff distance of 15.5 Å and a cubic spline width of 1.0 Å. All LJ parameters to model the framework atoms were taken from the Universal Force Field (UFF).

Section S2: Property characterizations

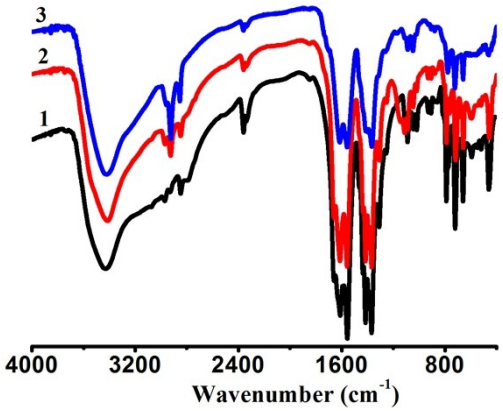


Fig. S1 IR spectra of **1-3**.

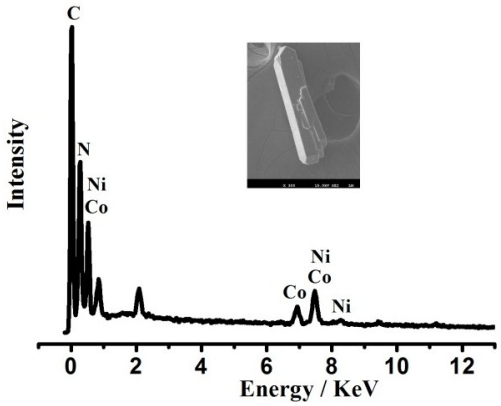


Fig. S2 SEM and EDS plot of **2**.

Table S1. The molar ratio of **2** product by ICP analysis.

complexe	the ratio by ICP analysis	the ratio by EDS analysis
2	Co/Ni 1.98 : 1.96	2.01 : 2.12

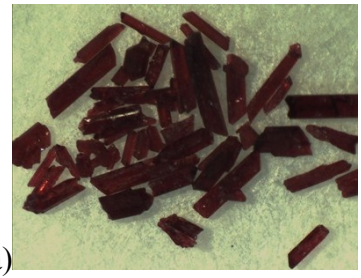
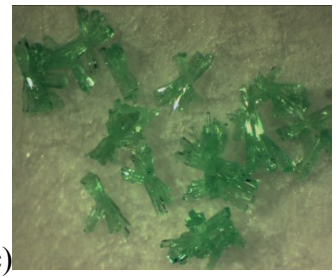
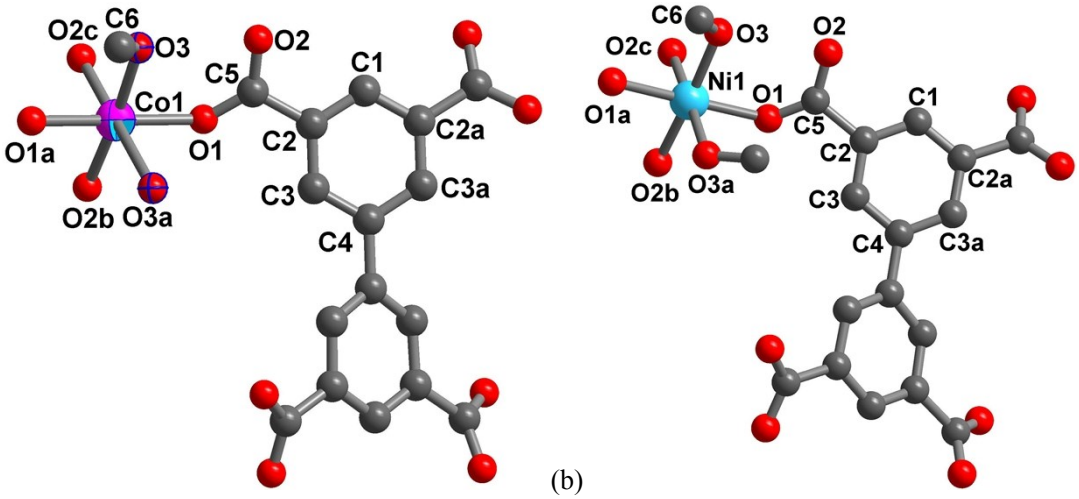
(a)  (b)  (c) 

Fig. S3 Photos of **1**−**3** showing regular color change from purple, red to green.



(a) (b)

Fig. S4 View of the coordination environment of metal atom in compound (a) **2**, (b) **3.**

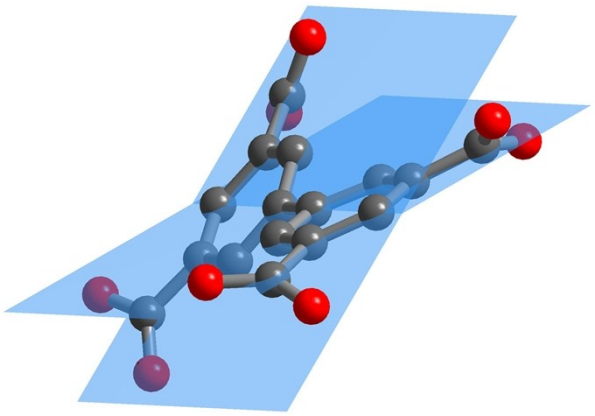


Fig. S5 View of the plane of two phenyl rings with dihedral angle 30.14°

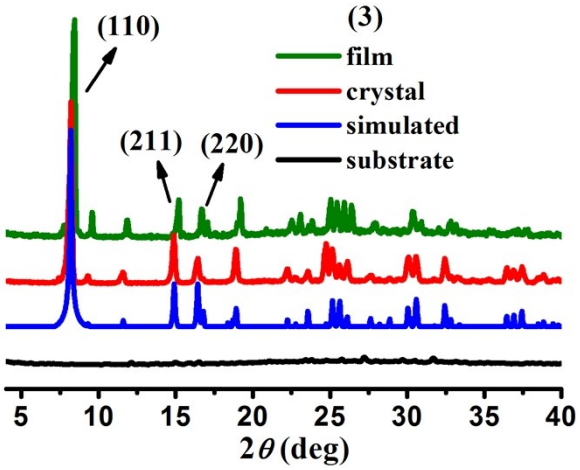


Fig. S6 PXRD patterns of the film, substrate, simulated and crystal for **3**.

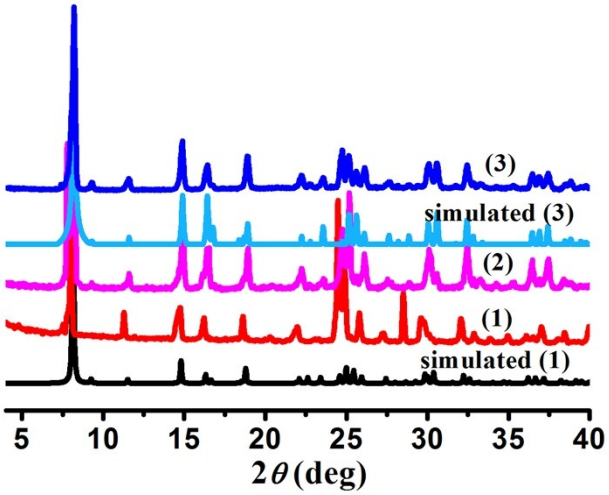


Fig. S7 PXRD patterns of the simulated and experimental for **1-3**.

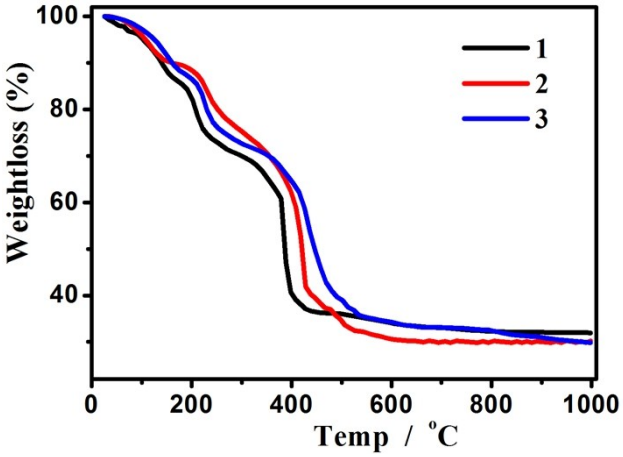


Fig. S8 The TGA plots of **1-3**.

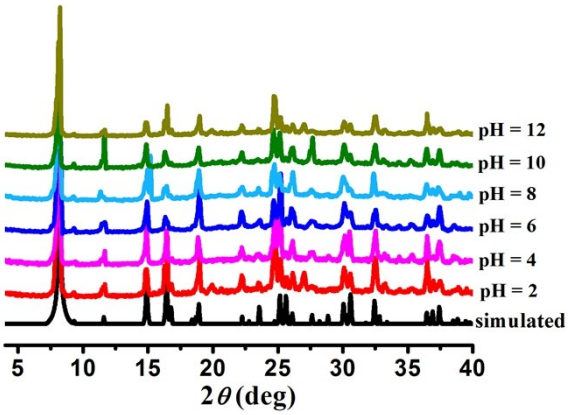


Fig. S9 PXRD patterns of **3** immersed in different *p*H values solutions.

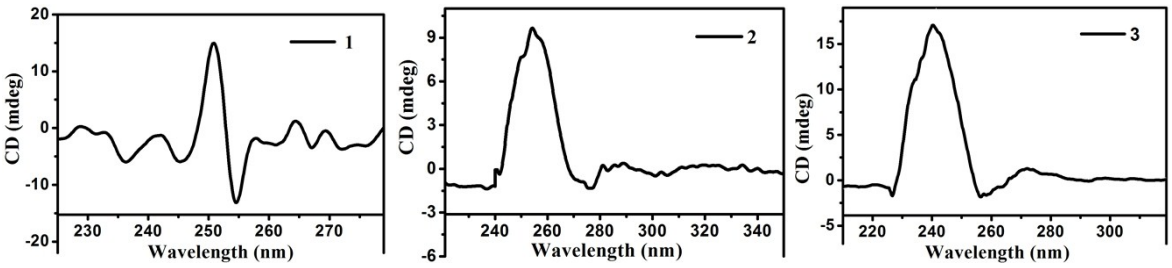


Fig. S10 The CD spectra of **1-3** in 5×10^{-5} mol/L aqueous solution at 298 K

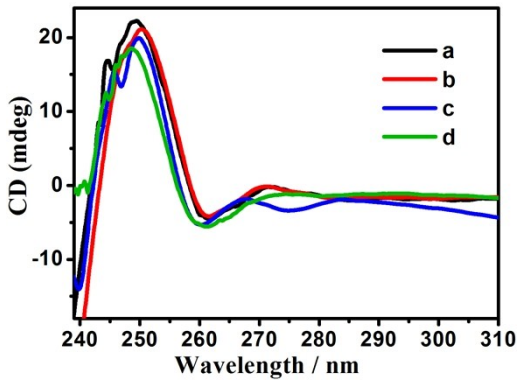


Fig. S11 Solid-state CD spectra of **1** from four batches

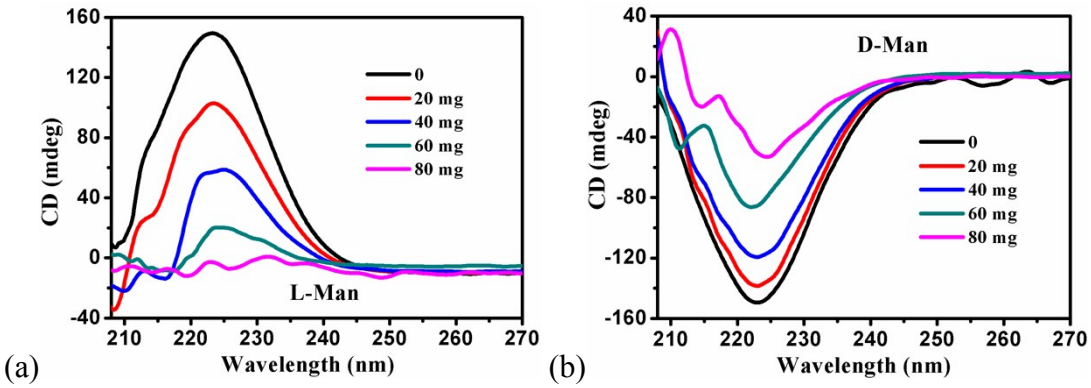


Fig. S12 CD spectra of (a) L-mandelic acid solution, (b) D-mandelic acid solution with different amounts of **1**

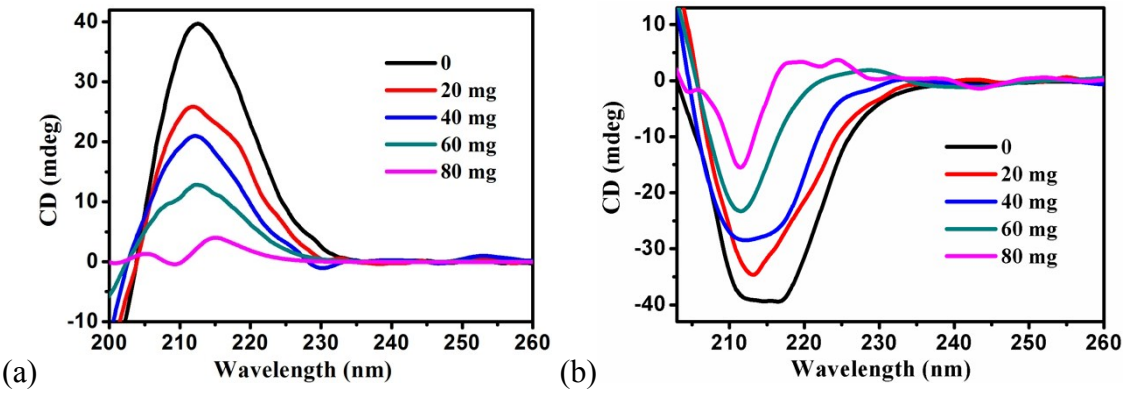


Fig. S13 CD spectra of (a) the L-histidine solution, (b) the D-histidine solution with different amounts of **1**

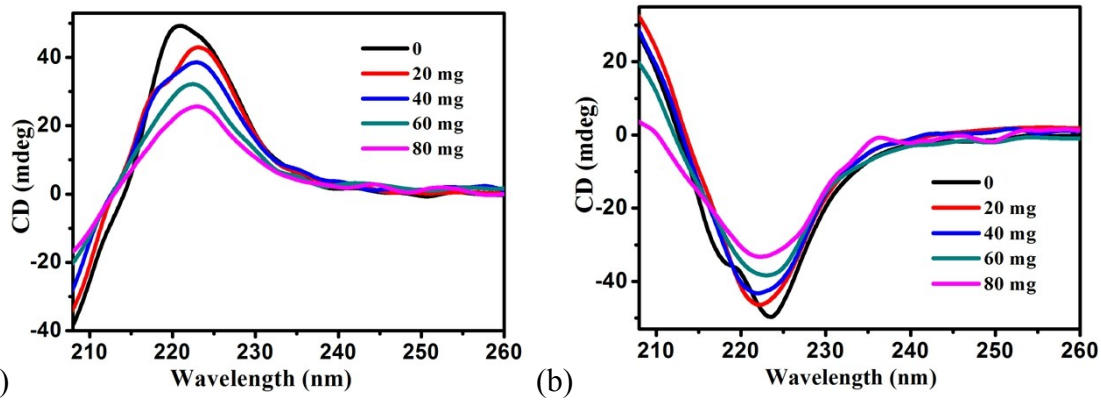


Fig. S14 CD spectra of (a) the L-tryptophan solution, (b) the D-tryptophan solution with different amounts of **1**

Section S3: Magnetic data

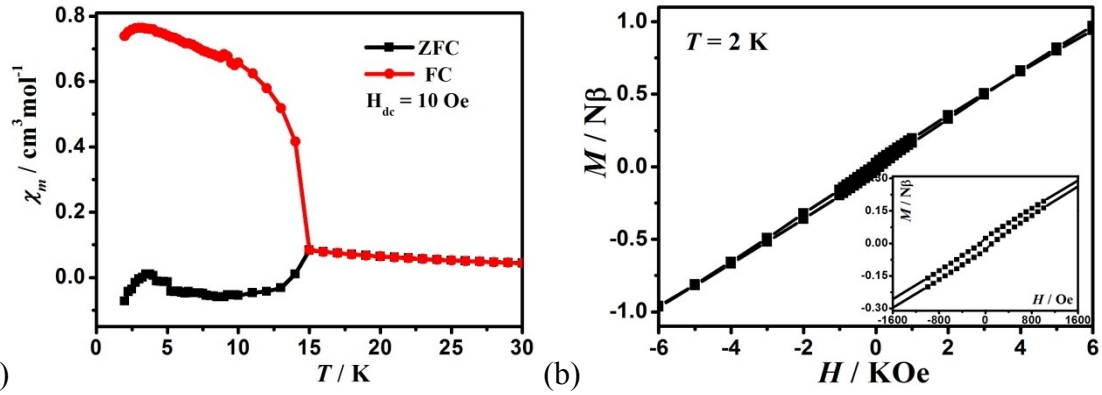


Fig. S15 (a) FC-ZFC magnetization at 10 Oe, (b) the hysteresis loop for **1**, inset: enlargement plot.

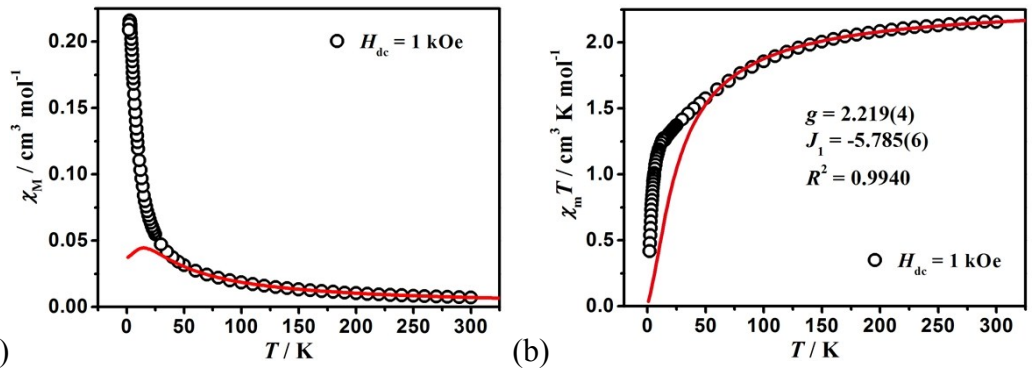
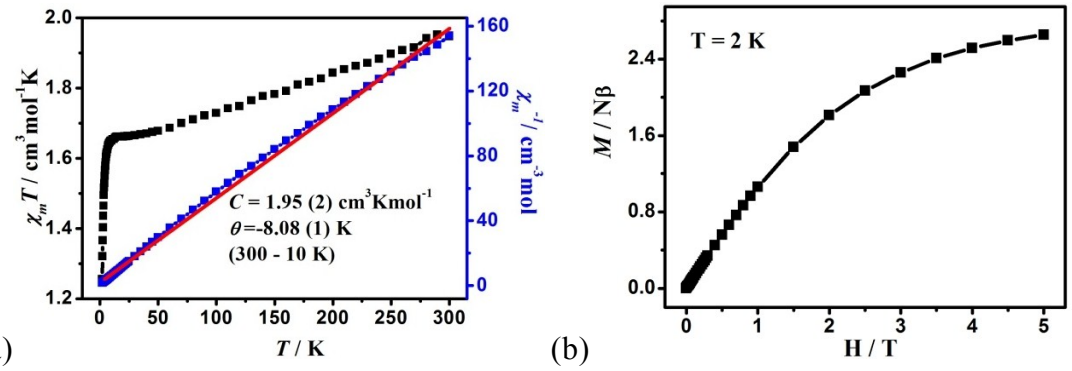
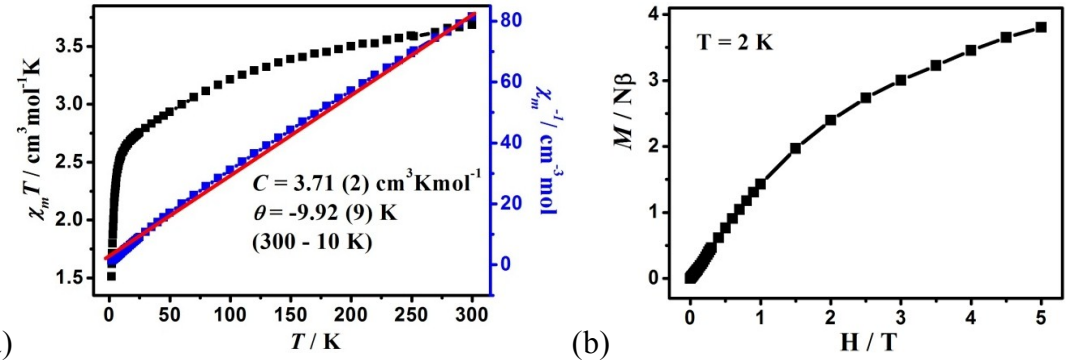


Fig. S16 (a) Magnetic fitting curve of χ_m vs T, (b) $\chi_m T$ vs T with Fisher model for **1**



(a) (b)

Fig. S17 (a) The $\chi_m T$ vs T plots and the Curie-Weiss fitting of χ_m^{-1} vs T curves for **3** in the range 10-300 K under an applied *dc* 1000 Oe field per Ni_2 unit, (b) field dependence of magnetization for **3** at 2 K.



(a) (b)

Fig. S18 (a) The $\chi_m T$ vs T plots and the Curie-Weiss fitting of χ_m^{-1} vs T curves for **2** in the range 10-300 K under an applied *dc* 1000 Oe field per CoNi unit, (b) field dependence of magnetization for **2** at 2 K.

Section S4: Crystal data of 1-3

Table S2. Crystal data and refinement parameters for compounds **1-3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{17}H_{14}Co_2O_{13}$	$C_{17.5}H_{14}CoNiO_{13}$	$C_{17}H_{14}Ni_2O_{13}$
Formula weight	542.14	553.90	541.66
Crystal system	tetragonal	tetragonal	tetragonal
Space group	$I4_122$	$I4_122$	$I4_122$
a (Å)	15.3341(2)	15.2512(5)	15.2538(1)
b (Å)	15.3341(2)	15.2512(5)	15.2538(1)
c (Å)	12.2106(2)	12.1084(5)	12.1148(2)
α(°)	90	90	90

β (°)	90	90	90
γ(°)	90	90	90
V(Å^3)	2871.14(7)	2816.4(2)	2818.85(6)
Z	4	4	4
ρ_{calc}(mg cm^{-3})	1.129	1.165	1.149
μ (mm^{-1})	1.190	5.791	1.371
F(000)	968.0	984.0	976.0
Crystal size (mm)	0.28 × 0.22 × 0.20	0.26 × 0.20 × 0.18	0.23 × 0.18 × 0.09
Reflections	13428	3197	3140
R_{int}	0.0185	0.0421	0.0306
Data/parameters	1801/67	1222/71	1394/71
S	1.102	1.080	1.167
R_1,wR_2 [$I > 2\sigma(I)$][a]	0.0469/0.1380	0.0944/0.2659	0.0275/0.0749
R_1,wR_2 (all data)[b]	0.0475/0.1391	0.0969/0.2698	0.0291/0.0757
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (eÅ^{-3})	0.82/-1.39	1.43/-2.77	0.37/-0.30
Flack parameter	0.220(19)	0.01(4)	0.081(14)

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b] $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S3. Selected bond length and bond angle for compounds **1-3**

Compound **1**			
Co(1)-O1	2.089(4)	Co(1)-O(2c)	2.045(3)
Co(1)-O(1a)	2.089(4)	Co(1)-O(3)	2.155(3)
Co(1)-O(2b)	2.045(3)	Co(1)-O(3d)	2.155(3)
O(1)-Co(1)-O(1a)	174.3(3)	O(3)-Co(1)-O(2d)	175.13(17)
O(1)-Co(1)-O(3)	83.32(16)	O(1a)-Co(1)-O(2d)	91.8(2)
O(1)-Co(1)-O(3b)	92.68(17)	O(1)-Co(1)-O(2c)	91.8(2)
O(1a)-Co(1)-O(3)	84.5(2)	O(2c)-Co(1)-O(3b)	175.13(17)
O(1a)-Co(1)-O(3b)	83.32(16)	O(3)-Co(1)-O(2c)	91.65(13)
O(3)-Co(1)-O(1a)	92.67(17)	O(2d)-Co(1)-O(3b)	91.65(13)

O(2c)-Co(1)-O(1a)	92.4(2)	O(3)-Co(1)-O(3b)	90.84(14)
O(1)-Co(1)-O(2d)	92.4(2)		

Symmetry codes: (a) 1/2-Y, -1/2+X, 1/2-Z; (b) 3/2-X, +Y, 1/2-X, 3/4-Z; (c) 1/2+Y, 1-X, -1/4+Z; (d) 1-Y, -1/2+X, 1/4+Z.

Compound **2**

M(1)-O(1)	2.021(6)	M(1)-O(2c)	2.075(6)
M(1)-O(1a)	2.021(6)	M(1)-O(3)	2.081(7)
M(1)-O(2b)	2.075(6)	M(1)-O(3c)	2.081(7)
O(1)-M(1)-O(1a)	85.5(4)	O(1a)-M(1)-O(3)	175.7(2)
O(1)-M(1)-O(2b)	89.8(4)	O(2c)-M(1)-O(2b)	176.4(4)
O(1a)-M(1)-O(2b)	92.9(4)	O(2b)-M(1)-O(3)	85.8(3)
O(1)-M(1)-O(2c)	92.9(4)	O(2c)-M(1)-O(3)	91.7(3)
O(1a)-M(1)-O(2c)	89.8(4)	O(2c)-M(1)-O(3b)	85.8(3)
O(1)-M(1)-O(3)	90.5(3)	O(2b)-M(1)-O(3b)	91.7(3)
O(1a)-M(1)-O(3b)	90.5(3)	O(3)-M(1)-O(3b)	93.6(4)
O(1)-M(1)-O(3b)	175.7(2)		

Symmetry codes: (a)1-Y, 1-X, 1-Z; (b)3/2-X, +Y,3/4-Z; (c)1-Y, -1/2+X, 1/4+Z.

Compound **3**

Ni(1)-O(1a)	2.068(2)	Ni(1)-O(2c)	2.027(2)
Ni(1)-O(1)	2.068(2)	Ni(1)-O(3)	2.079(2)
Ni(1)-O(2b)	2.027(2)	Ni(1)-O(3b)	2.079(2)
O(3b)-Ni(1)-O(3)	93.81(13)	O(1)-Ni(1)-O(2c)	92.35(13)
O(1a)-Ni(1)-O(3b)	91.82(11)	O(1)-Ni(1)-O(2b)	89.87(13)
O(1)-Ni(1)-O(3)	91.82(11)	O(1a)-Ni(1)-O(2b)	92.35(13)
O(1)-Ni(1)-O(3b)	86.12(12)	O(1a)-Ni(1)-O(2c)	89.87(13)
O(1)-Ni(1)-O(1a)	176.99(14)	O(2b)-Ni(1)-O(3)	175.36(8)
O(3)-Ni(1)-O(1a)	86.12(12)	O(2c)-Ni(1)-O(3b)	175.36(8)
O(2c)-Ni(1)-O(3)	90.62(10)	O(2c)-Ni(1)-O(2b)	84.99(13)

O(2b)-Ni(1)-O(3b)	90.62(10)

Symmetry codes: (a) 1/2-Y, 1/2-X, 3/2-Z; (b) 1/2-Y, +X, -1/4+Z; (c) 1/2-X, +Y, 7/4-Z.