Electronic Supplementary Material (ESI) for Dalton Transactions

Stepwise Replacement of Nickel with Cobalt Ions in a [Ni_6] Cluster

Graham N. Newton, Hiroki Sato, Takuya Shiga, and Hiroki Oshio*

Supplementary Information

Synthesis of H3L

1,3–Bis–(2–hydroxyphenyl)–1,3–propanedione (H_3L): Sodium hydride (6.4 g, 267 mmol) was suspended in 200 mL xylene, and 2–hydroxyacetophenone (4.53 g, 33 mmol) was added dropwise, followed by two drops of methanol and the resulting mixture brought to reflux for 10 minutes. Ethyl salicylate (4.53 g, 33 mmol) was then added dropwise and the reaction refluxed overnight. The yellow precipitate was then collected by vacuum filtration and washed with diethyl ether. The solid was then dissolved in 100 mL H_2O and 20 mL dilute HCl (approx. 5%) was added, resulting in precipation. The solid was collected and recrystallized from hot ethanol, yielding yellow crystalline 1,3–bis–(2–hydroxyphenyl)–1,3–propanedione (5.4 g, 21 mmol). ^{1}H NMR (400 MHz, D_6–Acetone): δ 2.80 (s, 2H, CH_2), 6.90 (m, 4H, ph), 7.25 (m, 2H, ph), 7.84 (m, 2H, ph).

Scheme S1: Structure of H3L.

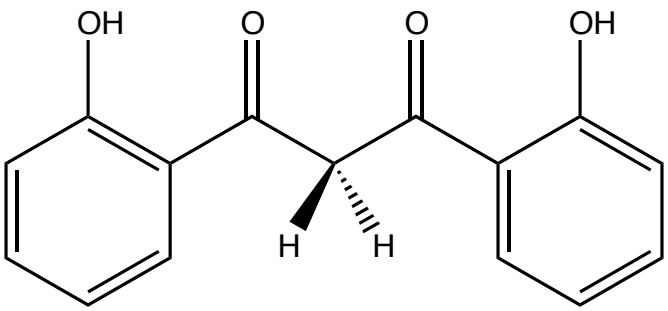

Table S1: Selected bonding distances and angles in **1**, **2** and **3**.

	Interaction	Distance (Å)	Interaction	Angle (°)
Complex **1**	Ni1–O6	2.006(6)	Ni2–O9–Ni3	99.5(2)
	Ni1–O3	2.014(6)	Ni2–O9–Ni1	95.8(2)
	Ni1–O4	2.020(6)	Ni3–O9–Ni1	95.9(2)
	Ni1–O10	2.022(6)	Ni1–O10–Ni2	95.8(2)
	Ni1–O7	2.024(6)	Ni1–O10–Ni2	96.4(2)
	Ni1–O9	2.098(6)	Ni2–O10–Ni2	97.6(2)
	Ni2–O8	1.994(6)	Ni1–O3–Ni3	97.8(3)
	Ni2–O7	2.005(6)	Ni2–O7–Ni1	96.8(2)
	Ni2–O9	2.010(6)	Ni2–O8–Ni3	96.4(2)
	Ni2–O10	2.039(6)		
	Ni2–O10	2.067(6)		
	Ni2–O13	2.120(6)		
	Ni3–O2	2.000(6)		
	Ni3–O9	2.026(6)		
	Ni3–O3	2.051(6)		
	Ni3–O12	2.063(7)		
	Ni3–O11	2.115(6)		
	Ni3–O8	2.135(6)		
Complex **2**	Ni1–O4	1.996(3)	Co1–O9–Ni2	99.27(15)
	Ni1–O3	2.005(2)	Co1–O9–Ni1	97.41(14)
	Ni1–O6	2.012(3)	Ni2–O9–Ni1	95.54(9)
	Ni1–O7	2.021(2)	Ni1–O10–Ni2	95.73(9)
	Ni1–O10	2.031(2)	Ni1–O10–Ni2	96.94(10)
	Ni1–O9	2.100(2)	Ni2–O10–Ni2	97.67(10)
	Ni2–O8	1.991(2)	Ni1–O3–Co1	98.31(15)
	Ni2–O7	2.013(2)	Ni2–O7–Ni1	96.82(10)
	Ni2–O9	2.029(2)	Ni2–O8–Co1	96.55(14)
	Ni2–O10	2.039(2)	Ni3–O9–Ni2	99.32(12)
	Ni2–O10	2.053(2)	Ni3–O9–Ni1	95.96(10)
	Ni2–O13	2.114(2)	Ni1–O3–Ni3	97.92(12)
	Ni3–O2	2.015(4)	Ni2–O8–Ni3	95.93(11)
	Ni3–O9	2.018(3)		
	Ni3–O12	2.053(3)		
	Ni3–O3	2.076(3)		
	Ni3–O8	2.160(3)		
	Ni3–O11	2.173(3)		
	Co1–O2	2.005(5)		
	Co1–O9	2.021(4)		
	Co1–O12	2.039(4)		
	Co1–O3	2.106(4)		
	Co1–O8	2.159(5)		
	Co1–O11	2.176(5)		
Complex **3**	Ni1–O4	1.994(3)	Co1–O9–Ni2	99.53(11)
	Ni1–O6	2.016(3)	Co1–O9–Ni1	96.79(11)
	Ni1–O3	2.017(3)	Ni2–O9–Ni1	95.56(11)
	Ni1–O7	2.032(3)	Ni1–O10–Ni2	95.81(10)
	Ni1–O10	2.037(3)	Ni1–O10–Ni2	97.43(12)
	Ni1–O9	2.116(3)	Ni2–O10–Ni2	97.84(11)
	Ni2–O8	1.995(3)	Ni2–O7–Ni7	96.62(11)
	Ni2–O7	2.020(3)	Ni1–O3–Co1	97.91(12)
	Ni2–O9	2.037(3)	Ni2–O8–Co1	96.06(11)
	Ni2–O10	2.040(3)		
	Ni2–O10	2.057(3)		
	Ni2–O13	2.123(3)		
	Co1–O2	2.021(3)		
	Co1–O9	2.027(3)		
	Co1–O12	2.063(3)		
	Co1–O3	2.091(3)		
	Co1–O8	2.174(3)		
	Co1–O11	2.198(3)		

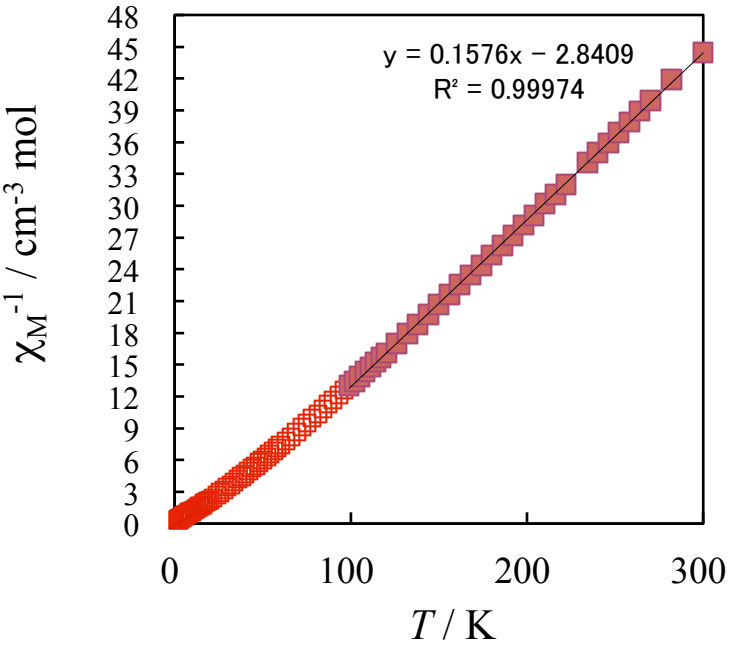

Figure S1: Curie-Weiss plot of **1**. A Weiss constant of +18.02 K was calculated from the line of best-fit.

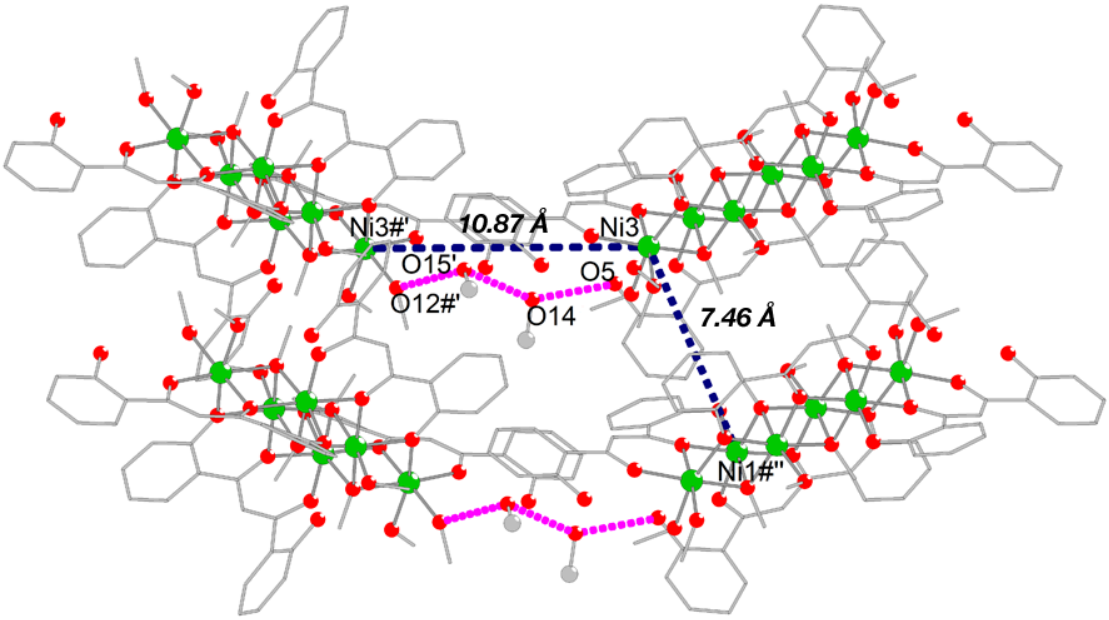

Figure S2: Four cluster units of **1**, illustrating the intermolecular interactions. Blue dashed lines are Ni···Ni distances and pink dashed lines illustrate the bydrogen bonded interactions between clusters and methanol molecules. Symmetry operators used in diagram: *-x, -y, 1-z*; #': *0.5-x, -0.5+y, 1.5-z*; #'': *-1-x, -y, 1-z*.

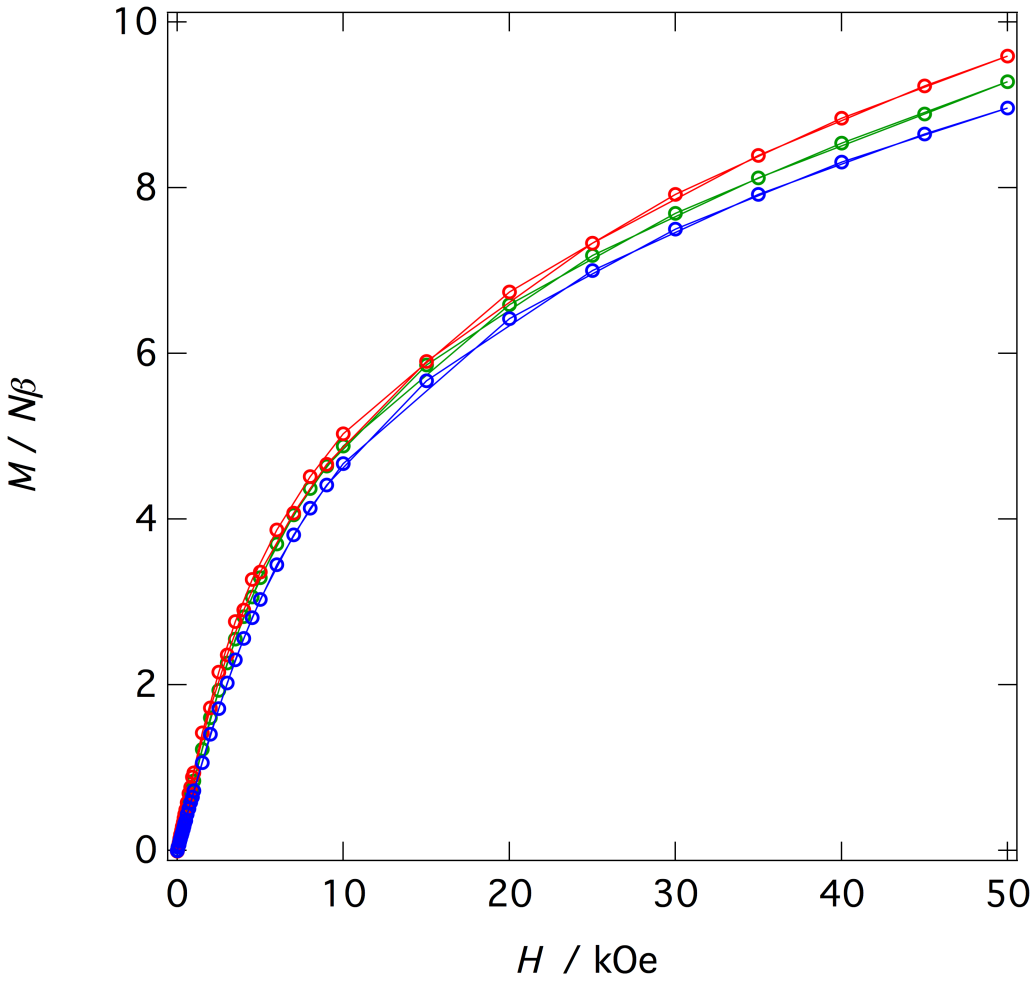

Figure S3: Field dependence of magnetisation plots of **1** (blue), **2** (green) and **3** (red).

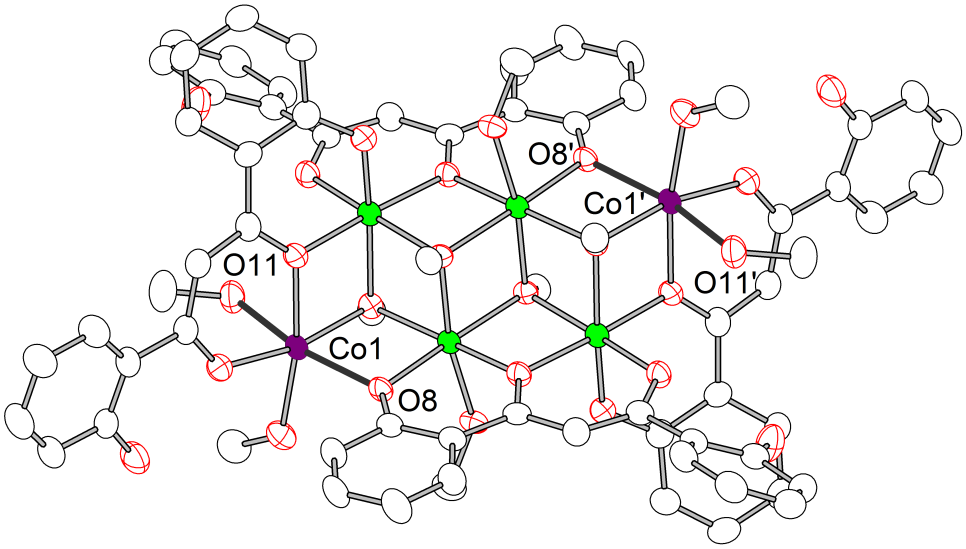

Figure S4: The elongation axes of the cobalt ions in complex **3**. Nickel ions in green, cobalt in purple, oxygen in red and carbon in white. The elongated Co–O bonds are shown in dark grey.