Electronic Supplementary Information for

Nuclearity Growth Towards Ni(II) Cubane in Self-Assembly with 2-Hydroxymethyl Pyridine (hmpH) and 5-Ethoxycarbonyl-2-hydroxymethyl Pyridine (5-ehmpH)

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Table S1 Selected bond distances (Å) and angles (°) for **1**

Ni(1)-O(1)	2.057(3)	Ni(1)-O(2)	2.052(3)
Ni(1)-N(1)	2.065(3)		
O(2)-Ni(1)-O(1)	88.33(12)	O(2)-Ni(1)-N(1)	92.22(12)
O(1)-Ni(1)-N(1)	78.70(12)	O(2)#1-Ni(1)-O(2)	86.64(17)
O(1)-Ni(1)-O(1)#1	96.76(16)	O(2)#1-Ni(1)-N(1)	99.45(13)
O(1)#1-Ni(1)-N(1)	90.61(11)		

Symmetry Code: #1: $-x + 1, y, -z + 1/2$.

Table S2 Selected bond distances (Å) and angles (°) for **2**

Ni(1)-O(1)	2.022(1)	Ni(1)-O(2)	2.029(1)
Ni(1)-O(3)	2.021(1)	Ni(1)-N(1)	2.049(2)
Ni(1)-O(5)	2.078(1)	Ni(1)-O(1)#1	2.107(1)
Ni(2)-O(6)#1	2.012(2)	Ni(2)-O(1)#1	2.016(1)
Ni(2)-O(2)	2.018(1)	Ni(2)-N(2)	2.036(2)
Ni(2)-O(2)#1	2.120(1)	Ni(2)-O(4)	2.123(1)
O(3)-Ni(1)-O(2)	92.63(6)	O(1)-Ni(1)-N(1)	80.82(6)
O(1)-Ni(1)-O(2)	87.95(6)	O(3)-Ni(1)-N(1)	99.12(6)
O(3)-Ni(1)-O(5)	100.99(6)	O(1)-Ni(1)-O(5)	92.44(6)
O(2)-Ni(1)-O(5)	85.07(6)	N(1)-Ni(1)-O(5)	91.81(6)
O(3)-Ni(1)-O(1)#1	90.48(6)	O(1)-Ni(1)-O(1)#1	76.19(6)
O(2)-Ni(1)-O(1)#1	84.81(5)	N(1)-Ni(1)-O(1)#1	95.88(6)
O(6)#1-Ni(2)-O(1)#1	94.22(6)	O(1)#1-Ni(2)-O(2)	87.52(6)
O(6)#1-Ni(2)-N(2)	99.05(6)	N(2)-Ni(2)-O(4)	87.44(6)
O(2)-Ni(2)-N(2)	80.96(6)	O(6)#1-Ni(2)-O(2)#1	90.34(6)
O(1)#1-Ni(2)-O(2)#1	85.66(5)	O(2)-Ni(2)-O(2)#1	75.91(6)
N(2)-Ni(2)-O(2)#1	99.72(6)	O(6)#1-Ni(2)-O(4)	103.06(6)
O(1)#1-Ni(2)-O(4)	84.16(6)	O(2)-Ni(2)-O(4)	90.94(6)
Ni(2)#1-O(1)-Ni(1)	92.95(6)	Ni(2)#1-O(1)-Ni(1)#1	91.26(6)
Ni(1)-O(1)-Ni(1)#1	103.20(6)	Ni(2)-O(2)-Ni(1)	93.49(6)
Ni(2)-O(2)-Ni(2)#1	103.38(6)	Ni(1)-O(2)-Ni(2)#1	89.71(6)

Symmetry Code: #1 $-x + 1$, y, $-z + 1/2$.

Table S3 Selected bond distances (Å) and angles (°) for **3**

Ni(1)-O(1)	2.063(6)	Ni(1)-N(2)	2.064(7)
Ni(1)-O(4)	2.069(6)	Ni(1)-N(1)	2.083(8)
Ni(1)-Br(1)	2.544(2)	Ni(1)-Br(2)	2.552(1)
Ni(2)-N(3)	2.061(7)	Ni(2)-O(7)	2.062(6)
Ni(2)-N(4)	2.076(7)	Ni(2)-O(10)	2.083(6)
Ni(2)-Br(2)	2.554(1)	Ni(2)-Br(1)	2.592(1)
O(1)-Ni(1)-N(2)	89.1(3)	O(1)-Ni(1)-O(4)	89.5(3)
N(2)-Ni(1)-O(4)	78.6(3)	O(1)-Ni(1)-N(1)	77.7(3)
O(4)-Ni(1)-N(1)	93.6(3)	N(2)-Ni(1)-Br(1)	94.6(2)
O(4)-Ni(1)-Br(1)	92.36(19)	N(1)-Ni(1)-Br(1)	98.8(2)
O(1)-Ni(1)-Br(2)	91.8(2)	N(2)-Ni(1)-Br(2)	99.5(2)
N(1)-Ni(1)-Br(2)	88.6(2)	O(7)-Ni(2)-N(4)	90.7(3)
Br(1)-Ni(1)-Br(2)	86.41(4)	N(3)-Ni(2)-O(7)	78.9(3)
N(3)-Ni(2)-O(10)	87.8(3)	O(7)-Ni(2)-O(10)	92.8(3)
N(4)-Ni(2)-O(10)	78.2(3)	N(3)-Ni(2)-Br(2)	98.6(2)
N(4)-Ni(2)-Br(2)	93.40(19)	Br(2)-Ni(2)-Br(1)	85.35(4)
O(10)-Ni(2)-Br(2)	93.89(17)	N(3)-Ni(2)-Br(1)	94.0(2)
O(7)-Ni(2)-Br(1)	88.0(2)	N(4)-Ni(2)-Br(1)	100.2(2)

Table S4 Selected bond distances (Å) and angles (°) for **4**

Ni(1)-O(1)	2.039(9)	Ni(1)-N(1)	2.048(8)
Ni(1)-O(4)	2.071(7)	Ni(1)-O(7)	2.069(9)
Ni(1)-N(3)	2.076(8)	Ni(1)-N(2)	2.086(8)
O(1)-Ni(1)-N(1)	78.8(3)	O(1)-Ni(1)-O(4)	93.1(4)
N(1)-Ni(1)-O(4)	93.2(3)	O(7)-Ni(1)-N(3)	79.4(3)
N(1)-Ni(1)-O(7)	93.9(3)	O(4)-Ni(1)-O(7)	88.0(3)
O(1)-Ni(1)-N(3)	100.6(3)	N(1)-Ni(1)-N(3)	97.5(3)
O(1)-Ni(1)-N(2)	92.4(3)	N(3)-Ni(1)-N(2)	93.4(3)
O(4)-Ni(1)-N(2)	77.7(3)	O(7)-Ni(1)-N(2)	94.9(3)

Table S5 Selected bond distances (Å) and angles (°) for **5**

Ni(1)-O(1)	2.044(2)	Ni(1)-O(1)#1	2.051(1)
Ni(1)-O(4)	2.060(2)	Ni(1)-N(1)	2.064 (2)
Ni(1)-O(1)#2	2.107(2)	Ni(1)-Br(1)	2.524(1)
O(1)-Ni(1)-O(1)#1	82.56(6)	O(1)-Ni(1)-O(4)	97.18(6)
O(1)#1-Ni(1)-O(4)	87.30(6)	O(1)-Ni(1)-N(1)	79.76(6)
O(4)-Ni(1)-N(1)	90.13(7)	N(1)-Ni(1)-O(1)#2	100.30(6)
O(1)-Ni(1)-O(1)#2	79.33(6)	O(1)#1-Ni(1)-O(1)#2	81.03(6)
O(1)#1-Ni(1)-Br(1)	99.36(4)	O(1)#2-Ni(1)-Br(1)	96.11(4)
O(4)-Ni(1)-Br(1)	87.80(5)	N(1)-Ni(1)-Br(1)	98.67(5)
Ni(1)-O(1)-Ni(1)#3	98.21(6)	Ni(1)-O(1)-Ni(1)#2	100.47(6)
Ni(1)#3-O(1)-Ni(1)#2	96.21(6)		

Symmetry Codes: #1: $-y + 5/4$, $x + 1/4$, $-z + 5/4$; #2: $-x + 1$, $-y + 3/2$, z.

Table S6 Selected bond distances (Å) and angles (°) for **6**

Ni(1)-O(9)	2.040(2)	Ni(1)-O(7)	2.047(2)
Ni(1)-O(4)	2.057(2)	Ni(1)-O(1)#1	2.066(2)
Ni(1)-N(1)	2.070(2)	Ni(1)-O(1)	2.104(2)
Ni(2)-O(1W)	2.015(2)	Ni(2)-O(8)	2.034(2)
Ni(2)-N(2)	2.058(2)	Ni(2)-O(1)	2.064(2)
Ni(2)-O(4)	2.068(2)	Ni(2)-O(4)#1	2.085(2)
O(9)-Ni(1)-O(7)	89.50(8)	O(9)-Ni(1)-O(4)	105.85(8)
O(7)-Ni(1)-O(4)	91.37(8)	O(9)-Ni(1)-O(1)#1	99.41(8)
O(4)-Ni(1)-O(1)#1	78.75(8)	O(1)#1-Ni(1)-N(1)	99.51(9)
O(9)-Ni(1)-N(1)	88.40(9)	O(7)-Ni(1)-N(1)	88.45(9)
O(7)-Ni(1)-O(1)	94.58(8)	O(4)-Ni(1)-O(1)	86.88(7)
O(1)#1-Ni(1)-O(1)	78.51(8)	N(1)-Ni(1)-O(1)	78.94(8)
O(1W)-Ni(2)-O(8)	95.01(9)	N(2)-Ni(2)-O(4)#1	100.12(8)
O(1W)-Ni(2)-N(2)	93.59(9)	O(8)-Ni(2)-N(2)	87.77(9)
O(1W)-Ni(2)-O(1)	98.53(8)	O(8)-Ni(2)-O(1)	93.04(8)
O(8)-Ni(2)-O(4)	94.78(8)	N(2)-Ni(2)-O(4)	80.09(8)
O(1)-Ni(2)-O(4)	87.64(7)	O(1W)-Ni(2)-O(4)#1	89.62(8)
O(1)-Ni(2)-O(4)#1	78.17(8)	O(4)-Ni(2)-O(4)#1	81.68(9)
Ni(2)-O(1)-Ni(1)#1	101.73(8)	Ni(2)-O(1)-Ni(1)	88.55(7)
Ni(1)#1-O(1)-Ni(1)	101.44(8)	Ni(1)-O(4)-Ni(2)	89.72(7)
Ni(1)-O(4)-Ni(2)#1	101.34(8)	Ni(2)-O(4)-Ni(2)#1	98.26(9)

Symmetry Codes: #1: $-x + 1, y, -z + 1/2$.

Figure S1. Crystal Structure of $[Ni_4(hmp)_4(\mu\text{-}OAc)_2(OAc)_2(MeOH)_2]\cdot 1.4(H_2O)$ with all disordered moieties, hydrogen atoms and solvent molecules omitted for clarity.

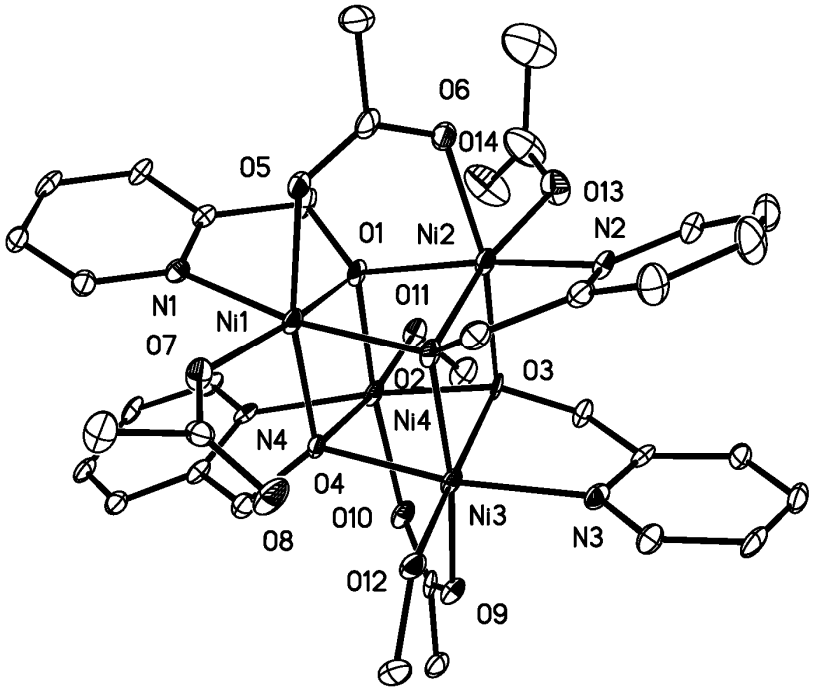

Table S7. Crystallographic data and structure refinement for $[Ni_4(hmp)_4(\mu\text{-}OAc)_2(OAc)_2(MeOH)_2]\cdot 1.4(H_2O)$

formula	$C_{34}H_{44}N_4Ni_4O_{15.4}$
fw	989.57
cryst. sys.	monoclinic
spacegroup	*C*2/c
a(Å)	39.642(6)
b(Å)	10.6741(15)
c(Å)	19.194(3)
α(°)	90
β(°)	94.065(4)
γ(°)	90
V(Å^3)	8102(2)
T/K	100(2)
Z	8
D_{calc}(g·cm^{-3})	1.623
μ(mm^{-1})	1.903
F_{000}	4088
collected reflns	22945
uniq. reflns	7141
R_{int}	0.0600
parameters	541
$R^a(I>2\sigma(I))$	0.0562
wR^b	0.1310
GOF^c	1.087
$\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ^{-3})	0.793 /–0.606

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = \{w\Sigma(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}\}^{1/2}$. [c] GOF $= \{\Sigma w(|F_o|-|F_c|)^2/(n-p)\}^{1/2}$, where *n* is the number of reflections and *p* is total number of parameters refined