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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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Self-assembly of NiX_2 (X = Br or OAc) with 2-hydroxymethyl pyridine (hmpH) and 5-ethoxycarbonyl-2-hydroxymethyl pyridine (5-ehmpH) results in six new Ni(II) complexes *viz.* $[Ni(hmpH)_2(H_2O)_2]Br_2$ (**1**), $[Ni_4(hmp)_4(\mu\text{-OAc})_4]$ (**2**), $[Ni_2(\mu\text{-Br})_2(5\text{-ehmpH})_4]Br_2 \cdot 0.33MeCN \cdot 0.67H_2O$ (**3**), $[Ni(5\text{-ehmpH})_3]Br_2 \cdot 0.33MeOH$ (**4**), $[Ni_4(5\text{-ehmp})_4(H_2O)_4Br_4]$ (**5**) and $[Ni_4(5\text{-ehmp})_4(\mu\text{-OAc})_2(OAc)_2(H_2O)_2]$ (**6**), all of which have different chemical compositions and structures. Complexes **2**, **5** and **6**, however, share a common cubane $[Ni_4O_4]$ core in which the deprotonated alkoxypyridine serves as a bridge-chelate. The others (*viz.* **1**, **3**, **4**) are mono- or dinuclear with the alkoxypyridine remaining in its native acid form.

Introduction

The coordination versatility of the simple ligand 2-hydroxymethyl pyridine (hmpH) (Chart 1) towards a wide range of transition metal ions has afforded a large family of structures, some of which are aesthetically complex,[1–7] show intriguing magnetic[1–12] and catalytic activities[13,14] as well as being biologically significant.[15] Additional hydroxymethyl group can also be introduced at the 6-position of the pyridine ring to give pyridine-2,6-diyldimethanol ($pdmH_2$) (Chart 1) which provides additional support for larger metal clusters.[3–6] Placement of a non-coordinating functionality on the hmpH ligand may affect the delocalization state of the pyridine ring, but it is generally deemed insufficient to alter the structural outcome of its self-assembly with metal ions.

It is important to put this assumption to test because in many supramolecular and MOF assemblies, spectator pendants are introduced to the spacers for different purposes. A better understanding of hmpH-type ligands is needed before more new architectural frameworks can be constructed. We herein report the synthesis of a new ligand 5-ethoxycarbonyl-2-hydroxymethylpyridine (5-ehmpH) (Chart 1) in which an electron withdrawing ester group is attached to the 5-position of the pyridine ring. The reactivity between hmpH and 5-ehmpH is compared by their reactions with two Ni(II) substrates *viz.* $NiBr_2$ and $Ni(OAc)_2$. Six new Ni(II) complexes have been isolated, namely: $[Ni(hmpH)_2(H_2O)_2]Br_2$ (**1**), $[Ni_4(hmp)_4(\mu\text{-OAc})_4]$ (**2**), $[Ni_2(\mu\text{-Br})_2(5\text{-ehmpH})_4]Br_2 \cdot 0.33MeCN \cdot 0.67H_2O$ (**3**), $[Ni(5\text{-ehmpH})_3]Br_2 \cdot 0.33MeOH$ (**4**), $[Ni_4(5\text{-ehmp})_4(H_2O)_4Br_4]$ (**5**) and $[Ni_4(5\text{-ehmp})_4(\mu\text{-OAc})_2(OAc)_2(H_2O)_2]$ (**6**). We herein report their synthesis and crystal structures.

Experimental

General

All chemicals and solvents used were of AR grade and purchased from commercial suppliers. They were used without further purification unless otherwise specified. ^1H NMR spectra were recorded on a Bruker ACF300 (300 MHz) NMR Spectrometer by using $CDCl_3$ or DMSO-d_6 as solvent. MS (ESI) experiments were performed on an LCQ ion-trap mass spectrometer. Infrared spectra were obtained on the Varian 3100 FT-IR spectrometer using KBr pellet. Crystallographic measurements were made on
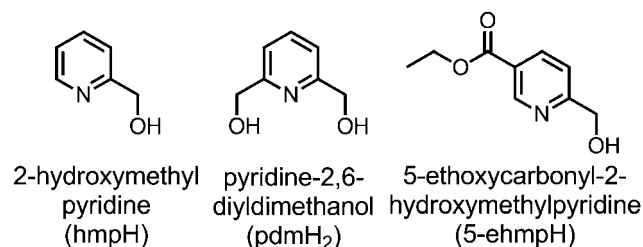
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† Dedicated to Professor Leonard F. Lindoy (University of Sydney) on the occasion of his 75th birthday.

‡ Electronic supplementary information (ESI) available: Bond distances and angles for **1–6**; structure and crystallographic parameters for $[Ni_4(hmp)_4(\mu\text{-OAc})_2(OAc)_2(MeOH)_2]\cdot1.4(H_2O)$. CCDC reference numbers 798244–798249 and 806741. For ESI and crystallographic data in CIF see DOI: 10.1039/c0ce00831a

Chart 1

a Bruker AXS APEX diffractometer by using graphite-monochromated Mo Kα (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS.[16] All crystal structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with SHELXTL-97 program.[17] In **1**, the hydrogen atoms on the OH group of the hmpH ligand as well as the coordinated water molecules were located from the difference Fourier map and refined with restraints in bond lengths (0.82 Å) and constraints in thermal parameters (U_{iso}(H) = 1.2U_{eq}(O)). In **3**, two free Br anions were disordered into two positions and were refined with disorder model. The hydrogen atoms in the OH group of 5-ehmpH ligand and free H_2O molecule could not be traced from difference Fourier map and therefore their coordinates were calculated by using the WinGX suite (Ver. 1.70.01).[18] These atoms were constrained to ride on their parent O atoms in the subsequent refinement with an O–H distance of 0.85 Å and thermal parameters of U_{iso}(H) = 1.2U_{eq}(O). In **4**, one of the [Ni-(5-ehmpH)$_3$]$^{2+}$ dications possesses higher symmetry than the molecule itself which has a meridional configuration. Such higher symmetry is suppressed in the refinement by treating this moiety using a disorder model. The hydrogen atoms in the OH group of the 5-ehmpH ligand were originally located from difference Fourier map but were subsequently constrained to ride on their parent O atoms for the following refinement with thermal parameters of U_{iso}(H) = 1.2U_{eq}(O). One of the free Br anions is disordered and refined with disorder model. The lattice MeOH molecule was refined with 0.5 site occupancy due to the high thermal parameters of its atoms and its hydrogen atoms could not be located. In **5** and **6**, the hydrogen atoms on coordinated

H_2O molecule were found in the difference Fourier map and refined freely (**5**) or with restraints applied to O–H distances (0.85 Å) (**6**). Their thermal parameters were fixed at U_{iso}(H) = 1.2U_{eq}(O). All non-hydrogen atoms were refined anisotropically. All other hydrogen atoms were calculated in ideal geometries and refined isotropically. A summary of the key crystallographic data for **1–6** is listed in Table 1.

2,5-Diethoxycarbonylpyridine

A solution of 2,5-pyridinedicarboxylic acid (1.67 g, 10 mmol) and *p*-toluenesulfonic acid monohydrate (4.00 g, 21 mmol) in EtOH (100 mL) was refluxed for 24 h. After removing the solvent, CHCl$_3$ followed by a saturated aqueous Na$_2$CO$_3$ (20 mL) were added and the mixture was washed with H_2O (4 times) and then dried over anhydrous Na$_2$SO$_4$. Removal of CHCl$_3$ afforded off-white powder of 2,5-diethoxycarbonylpyridine (1.67 g, 75%). ^{1}H NMR (CDCl$_3$): δ 9.32 (d, *J* = 2 Hz, 1H), 8.43 (d, *J* = 2 Hz, 1H), 8.20 (d, *J* = 2 Hz, 1H), 4.51 (q, *J* = 6 Hz, 2H), 4.45 (q, *J* = 6 Hz, 2H), 1.46 (t, *J* = 6 Hz, 3H), 1.43 (t, *J* = 6 Hz, 3H). MS (ESI) (*m/z*) (CHCl$_3$): 224.4 (M + H)$^+$, 246.4 (M + Na)$^+$. Anal. Calc. for C$_{11}$H$_{13}$NO$_4$: C, 59.19; H, 5.87; N, 6.27%. Found: C, 59.48; H, 5.93; N, 6.44%.

5-Ethoxycarbonyl-2-hydroxymethylpyridine (5-ehmpH)

To a degassed EtOH (75 mL) solution containing 2,5-diethoxycarbonylpyridine (1.67 g, 7.5 mmol) and NaBH$_4$ (0.19 g, 5.0 mmol) was slowly added CaCl$_2$ (0.83 g, 7.5 mmol) at 0 °C with stirring. After the addition was completed, the mixture was stirred for 2.5 h at the same temperature. The reaction

Table 1 Crystallographic data and structure refinement for **1–6**

	1	2	3	4	5	6
Formula	C$_{12}$H$_{18}$Br$_2$N$_2$NiO$_4$	C$_{32}$H$_{36}$N$_4$Ni$_4$O$_{12}$	C$_{110}$H$_{139}$Br$_{12}$N$_{13}$Ni$_6$O$_{38}$	C$_{82}$H$_{99}$Br$_6$N$_9$Ni$_3$O$_{28}$	C$_{36}$H$_{48}$Br$_4$N$_4$Ni$_4$O$_{16}$	C$_{44}$H$_{56}$N$_4$Ni$_4$O$_{22}$
fw	472.81	903.49	3562.52	2314.29	1347.26	1227.77
Cryst. Syst.	Monoclinic	Monoclinic	Triclinic	Monoclinic	Tetragonal	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*P*$\bar{1}$	*C*2	*I*4$_1$/*a*	*C*2/*c*
a/Å	20.5097(16)	17.2034(8)	13.7506(5)	28.336(6)	17.1496(4)	18.0337(19)
b/Å	7.9119(6)	12.6231(7)	22.6852(8)	8.9991(18)	17.1496(4)	20.674(2)
c/Å	12.3903(10)	16.8913(9)	25.2982(8)	21.869(4)	16.3976(8)	14.8310(16)
α/°	90	90	110.5250(10)	90	90	90
β/°	123.3340(10)	105.2340(10)	93.0870(10)	110.33(3)	90	109.676(2)
γ/°	90	90	105.9330(10)	90	90	90
V/Å^3	1679.8(2)	3539.2(3)	7007.1(4)	5229.1(18)	4822.7(3)	5206.6(9)
T/K	223(2)	100(2)	223(2)	100(2)	100(2)	100(2)
Z	4	4	2	2	4	4
D_{calcd}/g cm^{-3}	1.870	1.696	1.688	1.470	1.856	1.566
μ/mm^{-1}	5.927	2.163	4.289	2.899	4.920	1.507
F(000)	936	1856	3564	2344	2688	2544
No. of reflns collected	5721	12 360	76 088	18 890	16 743	18 401
No. of unique reflns	1929	4067	24 684	18 890	2765	5972
R_{int}	0.0289	0.0281	0.0826	0.0568	0.0286	0.0527
Parameters	105	237	1522	541	154	344
R^a	0.0357	0.0314	0.0693	0.0802	0.0264	0.0452
wR^b	0.089	0.0803	0.1866	0.1967	0.0679	0.1049
GOF^c	1.227	1.060	1.062	0.992	1.080	1.058
$\Delta\rho_{max}$/e Å^{-3}	0.690	0.761	3.549	1.775	0.802	0.700
$\Delta\rho_{min}$/e Å^{-3}	−0.671	−0.285	−1.582	−1.726	−0.254	−0.493

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} w$R_2 = \{w\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. ^{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.

was quenched by dropwise addition of concentrated H_2SO_4. White precipitate of $CaSO_4$ was filtered off, followed by solvent evaporation. Extraction of the resulting mixture with $CHCl_3$ and H_2O, followed by solvent evaporation gave pale yellow solid of 5-ethoxycarbonyl-2-hydroxymethylpyridine (0.94 g, 69%). ^{1}H NMR ($CDCl_3$): δ 8.85 (s, 1H), 8.07 (d, J = 8 Hz, 1H), 7.34 (d, J = 8 Hz, 1H), 5.26 (s, 1H), 4.65 (s, 2H), 4.20 (q, J = 7 Hz, 2H), 1.21 (t, J = 7 Hz, 3H). MS (ESI) (m/z) ($CHCl_3$): 182.3 (M + H)[+], 204.1 (M + Na). Anal. Calc. for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73%. Found: C, 60.01; H, 6.35; N, 7.92%.

[Ni(hmpH)$_2$(H$_2$O)$_2$]Br$_2$ (1)

$NiBr_2$ (0.22 g, 1 mmol) in MeOH (5 mL) was mixed with hmpH (0.24 g, 2.2 mmol) in MeCN (5 mL). The resulting royal-green solution was stirred for 4 h at rt. Royal-green crystals of the title compound were obtained by slow diffusion of Et_2O vapour into the resulting solution over 2 weeks (0.35 g, 75%). ^{1}H NMR (DMSO-d_6): δ 8.77 (d, J = 5 Hz, 1H), 8.57 (t, J = 8 Hz, 1H), 8.01 (d, J = 8 Hz, 1H), 7.92 (t, J = 6 Hz, 1H), 4.87 (s, 2H), 4.32 (s, 2H). Anal. Calc. for $C_{12}H_{18}Br_2N_2NiO_4$: C, 30.49; H, 3.84; N, 5.93%. Found: C, 30.01; H, 3.59; N, 5.80%. IR (KBr): 1612 (C=N$_{pyr}$), 1442 (C=C$_{pyr}$), 1046 (C–O) cm^{-1}.

[Ni$_4$(hmp)$_4$(μ-OAc)$_4$] (2)

$Ni(OAc)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) in MeOH (5mL) was mixed with hmpH (0.12 g, 1.1 mmol) in MeCN (5 mL). The resulting dark green solution was stirred for 4 h at rt. Dark green crystals of the title compound were obtained by slow diffusion of Et_2O vapour into the resulting solution over 1 week (0.12 g, 40%). ^{1}H NMR for this complex cannot be done due to its strong paramagnetic nature. Anal. Calc. for $C_{16}H_{20}N_2NiO_6$: C, 42.54; H, 4.02; N, 6.20%. Found: C, 41.82; H, 4.50; N, 5.98%. IR (KBr): 1570 (very broad peak) (C=N$_{pyr}$ and conjugated C–O in CH_3COO), 1416 (C=C$_{pyr}$), 1049 (C–O) cm^{-1}.

[Ni$_2$(μ-Br)$_2$(5-ehmpH)$_4$]Br$_2 \cdot$0.33MeCN$\cdot$0.67H$_2$O (3)

$NiBr_2$ (0.22 g, 1 mmol) in MeOH (5 mL) was mixed with a mixture of 5-ethoxycarbonyl-2-hydroxymethylpyridine (0.40 g, 2.2 mmol) in MeCN (5 mL). The resulting dark-blue solution was stirred for 4 h at rt. Dark-blue crystals of the title compound were obtained by slow diffusion of Et_2O vapour into the resulting solution over 2 weeks (0.42 g, 69%). ^{1}H NMR (DMSO-d_6): δ 8.98 (s, 1H), 8.34 (s, 1H), 7.66 (s, 1H), 4.89 (s, 1H), 4.64 (s, 2H), 4.34(s, 2H), 1.32 (s, 3H). Anal. Calc. for $C_{36.66}H_{46.33}Br_4N_{4.33}Ni_2O_{12.66}$: C, 37.09; H, 3.93; N, 5.11%. Found: C, 38.91; H, 4.02; N, 4.76%. IR (KBr): 1729 (C=O), 1611 (C=N$_{pyr}$), 1427 (C=C$_{pyr}$), 1038 (C–O) cm^{-1}.

[Ni(5-ehmpH)$_3$]Br$_2 \cdot$0.33MeOH (4) and [Ni$_4$(5-ehmp)$_4$(H$_2$O)$_4$Br$_4$] (5)

$NiBr_2$ (0.22 g, 1 mmol) in MeOH (5mL) was mixed with a mixture of 5-ehmpH (0.20 g, 1.1 mmol) in MeCN (5 mL). The resulting dark-blue solution was stirred for 4 h at rt. Blue crystals of 4 (0.26 g, 26%) and dark-green crystals of 5 (trace amount) were obtained by slow diffusion of Et_2O vapour into the resulting solution over 2 weeks. ^{1}H NMR (DMSO-d_6) for 4: δ 8.98 (s, 1H),

8.28 (s, 1H), 7.63 (s, 1H), 4.89 (s, 1H), 4.63 (s, 2H), 4.32 (s, 2H), 1.32 (s, 3H). Anal. Calc. for $C_{27.33}H_{34.32}Br_2N_3NiO_{9.33}$ (4): C, 42.48; H, 4.48; N, 5.44%. Found: C, 41.82; H, 4.50; N, 5.98%. IR (KBr) for 4: 1715 (C=O), 1613 (C=N$_{pyr}$), 1456 (C=C$_{pyr}$), 1038 (C–O) cm^{-1}.

## [Ni$_4$(5-ehmp)$_4$(μ-OAc)$_2$(OAc)$_2$(H$_2$O)$_2$] (6)

$Ni(OAc)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) in MeOH (5 mL) was mixed with 5-ethoxycarbonyl-2-hydroxymethylpyridine (0.20 g, 1.1 mmol) in MeCN (5 mL). The resulting blue solution was stirred for 4 h at rt. Blue crystals of the title compound were obtained by slow diffusion of ether vapour into the resulting solution over 3 weeks (0.85 g, 69%). ^{1}H NMR analysis could not be done for this complex due to its strong paramagnetic nature. Anal. Calc. for $C_{44}H_{56}N_4Ni_4O_{22}$: C, 43.05; H, 4.60; N, 4.56%. Found: C, 42.36; H, 4.41; N, 4.40%. IR (KBr): 1715 (C=O), 1610 (C=N$_{pyr}$), 1421 (C=C$_{pyr}$), 1039 (C–O) cm^{-1}.

Results and discussion

Synthesis

The synthesis of 5-ehmpH ligand follows the synthetic procedures reported by Kojima *et al.* in their preparation of 4-ethoxycarbonyl-2-hydroxymethylpyridine (4-ehmpH).[19] As shown in Scheme 1, the first step involves the acid catalyzed esterification of 2,5-pyridinedicarboxylic acid with ethanol to form 2,5-diethoxycarbonylpyridine. The ester group at 2-position is then reduced by ethanolic $NaBH_4$ to give the targeted 5-ehmpH in 52% overall yield.

The ^{1}H NMR spectra of 5-ehmpH and hmpH in $CDCl_3$ show that the OH group in 5-ehmpH is more acidic (5.26 ppm for 5-ehmpH vs. 4.96 ppm for hmpH). For a direct comparison of the reactivity between the two ligands, we carried out reactions of hmpH and 5-ehmpH with NiX_2 (X = Br and OAc) under similar reaction conditions. As shown in Scheme 2, reactions of hmpH and 0.5 eq. $NiBr_2$ in a solvent mixture of MeOH/MeCN gave rise to an ionic aqua complex [Ni(hmpH)$_2$(H$_2$O)$_2$]Br$_2$ (1) in 75% yield. Adjusting the metal-to-ligand ratio to 1 : 1 also yielded complex 1, but in a lower yield (38%). Similar reaction using hmpH and $Ni(OAc)_2 \cdot 4H_2O$ in 2 : 1 and 1 : 1 molar ratio afforded two stoichiometrically directed neutral complexes [Ni(hmpH)$_2$(OAc)$_2$] (71% yield)[20] and [Ni$_4$(hmp)$_4$(μ-OAc)$_4$] (2) (40% yield) respectively. Further reaction of [Ni(hmpH)$_2$(OAc)$_2$] with 1 equivalent of $Ni(OAc)_2 \cdot 4H_2O$ in a dilute MeCN/MeOH (1 : 1, v/v) solution yielded [Ni$_4$(hmp)$_4$(μ-OAc)$_2$(OAc)$_2$(MeOH)$_2$]$\cdot$1.4(H$_2$O) (ESI) whose structure is closely related to the reported complex [Ni$_4$(hmp)$_4$(μ-OAc)$_2$(OAc)$_2$(H$_2$O)$_2$]$\cdot$2.25(H$_2$O)$\cdot$0.5(1,4-dioxane).[20]
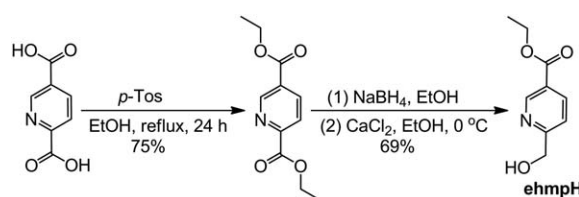
Scheme 1 Two-step synthesis of 5-ehmpH.
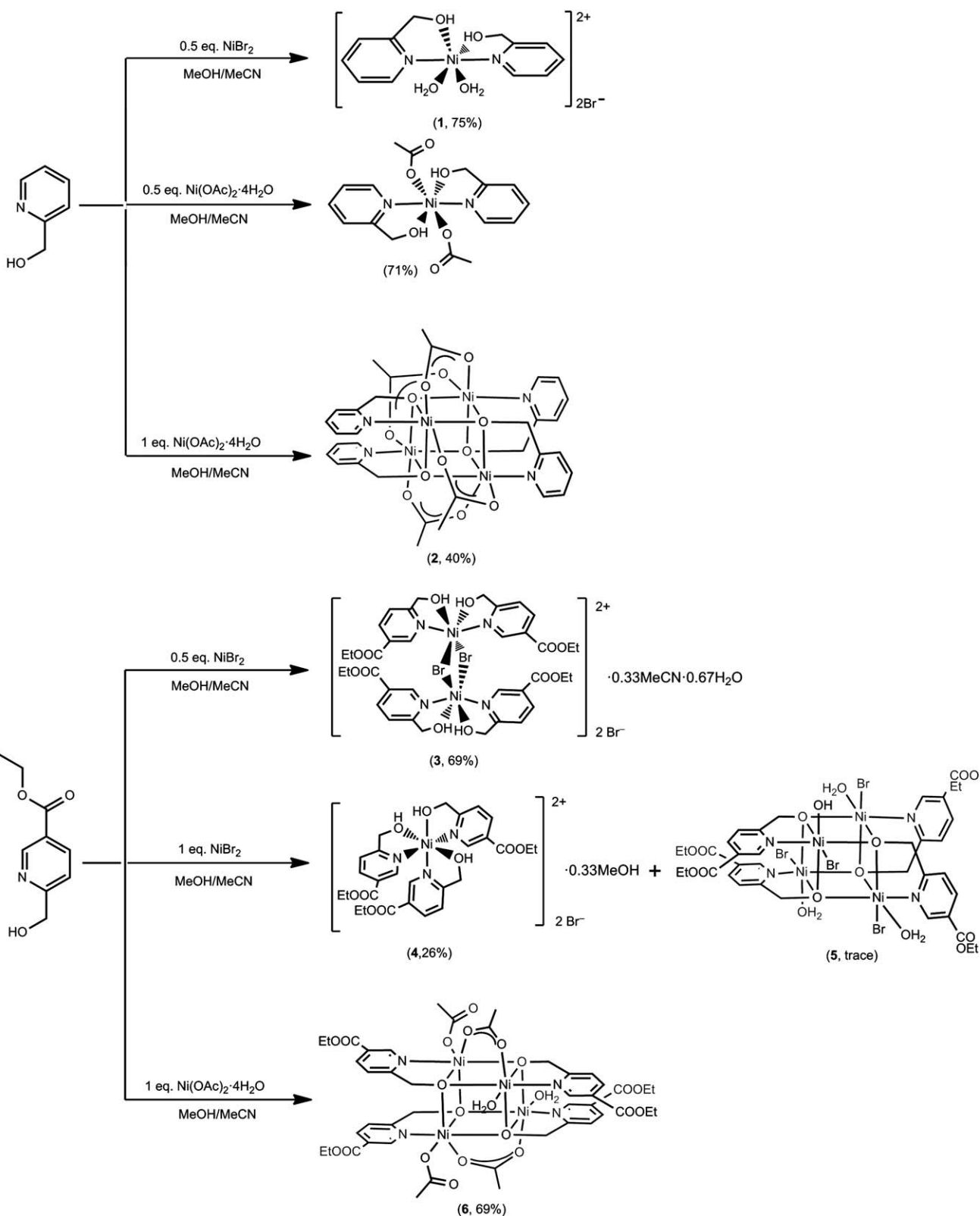
Scheme 2 Synthetic schemes for complexes 1–6.

Addition of 5-ehmpH to $NiBr_2$ in a 2 : 1 ratio leads to the formation of a dinuclear compound $[Ni_2(\mu-Br)_2(5-ehmpH)_4]Br_2\cdot0.33MeCN\cdot0.67H_2O$ (**3**) (69% yield) while a 1 : 1 molar ratio reaction yields a mononuclear binary complex [Ni(5-ehmpH)$_3$]Br$_2\cdot$0.33MeOH (**4**) (26% yield) accompanied by trace amount of [Ni$_4$(5-ehmp)$_4$(H$_2$O)$_4$Br$_4$] (**5**). Finally, reactions of

5-ehmpH with $Ni(OAc)_2 \cdot 4H_2O$ in a 2 : 1 and 1 : 1 molar ratio both lead to the formation of the same complex $[Ni_4(5\text{-}ehmp)_4(\mu\text{-}OAc)_2(OAc)_2(H_2O)_2]$ (6) with 10% (based on Ni) and 69% yields respectively.

Complexes 1–6 are stable toward air and moisture and are soluble in common solvents such as MeCN, MeOH, DMF and DMSO. The paramagnetic nature of octahedral Ni(II) precluded the ^1H NMR analysis of 2 and 6. Others could be recorded but of poor quality. Complexes 2–6 were characterized by means of IR and single-crystal X-ray crystallographic analysis.

Crystal structures

[Ni(hmpH)$_2$(H$_2$O)$_2$]Br$_2$ (1). Complex 1 crystallizes in the monoclinic space group $C2/c$. Its asymmetric unit contains half of the $[Ni(hmpH)_2(H_2O)_2]^{2+}$ dications and one Br anion. As shown in Fig. 1, the Ni(II) center lies on a twofold axis and is associated by two neutral hmpH ligands coordinated with nitrogen *trans* and oxygen *cis* to each other. The octahedral geometry of the Ni(II) center is completed by further coordination of two aqua molecules *trans* to the OH group of hmpH. This structure is similar to those of $M(hmpH)_2(sac)_2$ (M = Co, Ni; sac = saccharinate)[21] and $[Ni(hmpH)_2(H_2O)_2]Cl_2$.[22] Its respective Ni–N (2.065(3) Å) and Ni–O$_{hmpH}$ bond lengths (2.057(3) Å) are slightly shorter than those in $Ni(hmpH)_2(sac)_2$ (av. 2.089 Å for Ni–N$_{hmpH}$ and av. 2.102 Å for Ni–O$_{hmpH}$)[21] but comparable to those found in $[Ni(hmpH)_2(H_2O)_2]Cl_2$ (2.063(1) Å for Ni–N and 2.057(1) Å for Ni–O$_{hmpH}$).[22]

Intermolecular O–H···Br hydrogen bonding between the H atoms of the OH group of hmpH ligand with Br (H···Br 2.38 Å, O–H···Br 177.7°) together with hydrogen bonding between the coordinated water and Br (H···Br 2.51 Å, O–H···Br 149.5°; H···Br 2.46 Å, O–H···Br 165.1°) resulted in a two dimensional network extended in the bc plane (Fig. 2).

[Ni$_4$(hmp)$_4$(μ-OAc)$_4$] (2). Complex 2 crystallizes in the monoclinic space group $C2/c$ as tetranuclear $[Ni_4(hmp)_4(\mu\text{-}OAc)_4]$ with a distorted cubane core of $[Ni_4O_4]$. The oxygen atoms in this core come from the alkoxide of hmp (Fig. 3). The aggregate is strengthened by four bridging acetate on the four faces of the cube. The Ni···Ni contacts on these faces are significantly shorter (2.927–2.947 Å; av. 2.937 Å) than those on the other two faces without the μ-OAc support (3.236–3.248 Å; av. 3.242 Å). These distances are similar to those found in $[Ni_4(\mu\text{-}OAc)_2(OAc)_2(hmp)_4(H_2O)_2]$ (av. 2.923 Å vs. av. 3.194 Å).[20] The pyridyl nitrogen of hmp completes the octahedral sphere of Ni(II). The cubane core structure of 2 resembles those found in
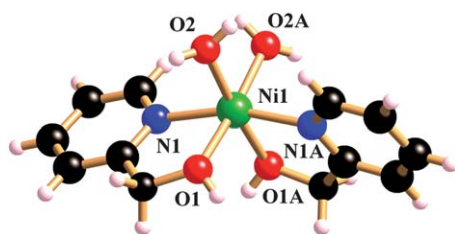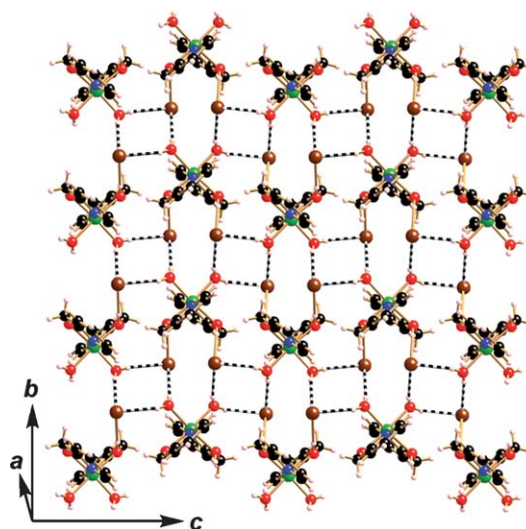

Fig. 2 Extended network of 1 in *bc* plane.

$[Co_4(hmp)_4Cl_4(H_2O)_3(MeOH)]$,[1] $[Ni(hmp)(MeOH)Cl]_4$,[22] and other heterometallic aggregates such as $[Mn_3Ni(hmp)_3(\mu_3\text{-}O)(N_3)_3(C_7H_5O_2)_3]$ and $[Mn_3Zn(hmp)_3(\mu_3\text{-}O)(N_3)_3(C_3H_5O_2)_3]$.[23]

A distinctive feature of 2 is that the dihedral angles within the two nearly perpendicular hmp pairs are significantly different (20.4° and 57.1°) although the coordination environments of the four hmp ligands are similar (Fig. 3b and c).

[Ni$_2$(μ-Br)$_2$(5-ehmpH)$_4$]Br$_2$·0.33MeCN·0.66H$_2$O (3). Complex 3 crystallizes in the triclinic space group $P\bar{1}$ and its asymmetric unit contains three unique dinuclear $[Ni_2(\mu\text{-}Br)_2(5\text{-}ehmpH)_4]^{2+}$ dications, six free bromide atoms of which two are disordered, one MeCN and two water molecules. As shown in Fig. 4, the dinuclear dicationic fragment does not exhibit any inversion center or mirror plane as a result of the randomly posed ethyl groups. Each Ni(II) is associated with two 5-ehmpH chelates in similar fashion to that in 1, i.e. *trans*-nitrogen donors and *cis*-oxygen donors. Such structural feature is found in the hmpH analogues of Co(II),[24] Zn(II),[25] and Mn(II)[26] but surprisingly opposite from its Ni(II)-hmpH derivative $[Ni_2(\mu\text{-}Cl)_2(hmpH)_4]^{2+}$ in which the N donors are *cis* to each other whereas the OH are *trans* to each other.[14] Unlike 1, the remaining two sites are taken up by bridging Br, which are *trans* to OH groups, resulting in a dinuclear octahedral framework. The Ni–N (av. 2.072 Å) and Ni–O (av. 2.069 Å) bond distances are slightly longer than those found in 1 (2.065(3) Å for Ni–N and 2.057(3) Å for Ni–O). This could be attributed to the slightly weaker σ-donating power of 5-ehmpH due to the presence of the electron-withdrawing ester group. This could also explain why Ni(II) prefers to pick up a stronger donor such as bromide to achieve stabilization. The Ni–N and Ni–O lengths are also slightly weaker than those in $[Ni_2(\mu\text{-}Cl)_2(hmpH)_4]^{2+}$ (av. 2.062 Å for Ni–N and av. 2.065 Å for Ni–O).[14]

[Ni(5-ehmpH)$_3$]Br$_2$·0.33MeOH (4). Complex 4 crystallizes in the monoclinic space group $C2$ and its asymmetric unit contains one and a half $[Ni(5\text{-}ehmpH)_3]^{2+}$ dications, three Br anions, and half MeOH molecule. The cationic fragment consists of

Fig. 1 Structure of $[Ni(hmpH)_2(H_2O)_2]^{2+}$ dications in 1 with labeling scheme. The dissociated Br anions are omitted for clarity.
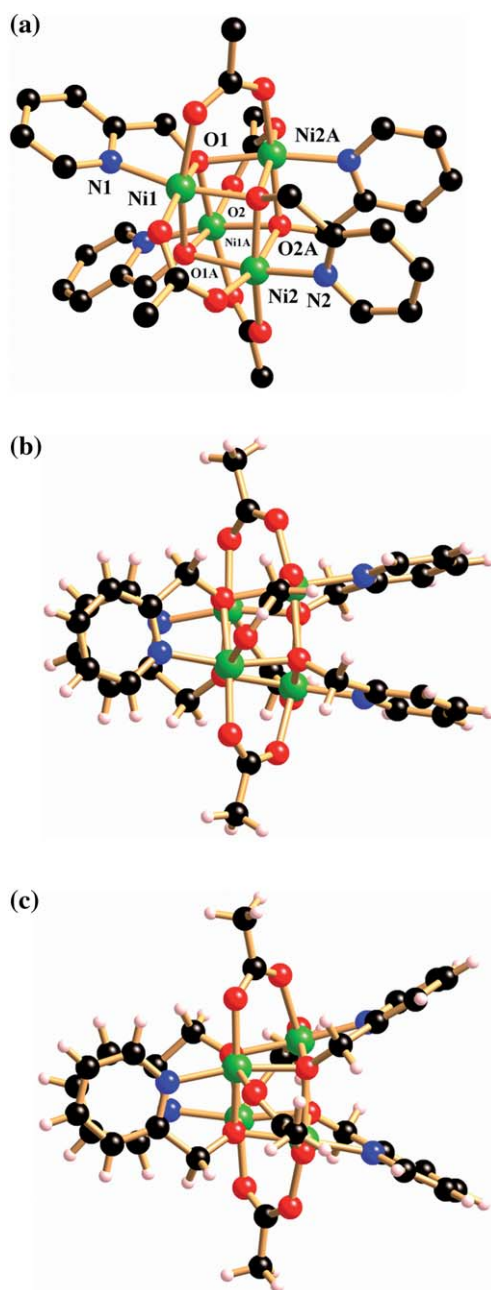
Fig. 3 Crystal structure of **2**: (a) with labeling scheme and all hydrogen atoms were omitted for clarity. (b and c) showing one pair of staggered hmp and the other pair of hmp with dihedral angle of 20.4° and 57.1°, respectively.

a mononuclear Ni(II) with three chelating 5-ehmpH ligands coordinated in an asymmetric meridional fashion (Fig. 5). In this mode, it keeps a pair of *trans*-oriented nitrogen donors as in **1** and **3**. The remaining two sites are occupied by a chelating 5-ehmpH, thus resulting in another pair of *trans*-oxygen donors (Ni1–O1 and Ni1–O7). In the coordination sphere, one of the chelates appears to be more strongly bound than the other two, as evident in the shorter Ni1–O1 (2.039(9) Å) and Ni1–N1 (2.048(8) Å) bonds compared with the others (Ni1–O4 and Ni1–O7 2.071(7) and 2.069(9) Å; Ni1–N2 and Ni1–N3 2.086(8) and 2.075(8) Å).
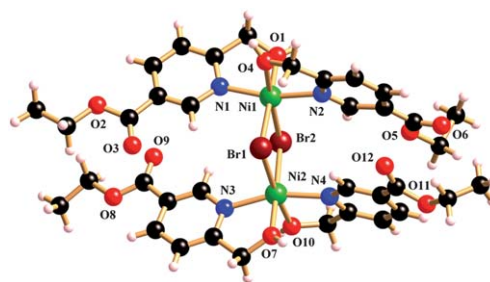

Fig. 4 Molecular view of a dicationic moiety in **3** with labeling scheme. Other fragments, Br anions and solvents were omitted for clarity.

[Ni₄(5-ehmp)₄(H₂O)₄Br₄] (5). Complex **5** crystallizes in the tetragonal space group $I4_1/a$. Its structure consists of a tetranuclear [Ni₄(5-ehmp)₄(H₂O)₄Br₄] cubane aggregate with a similar core as **2** (Fig. 6a). There are, however, notable differences in the peripheral donors. The four bridging acetates in **2** are replaced by four terminal bromides and four terminal aqua.

The four 5-ehmp ligands are oriented as two nearly perpendicular pairs (Fig. 6b). Such configuration of the 5-ehmp ligand pairs is found in most cubane structures supported by its hmp counterparts such as **2**. However, in **5**, each pair of the 5-ehmp ligands is nearly parallel to each other (dihedral angle 13.5°) and adopt staggered configurations, result in significant π–π interactions (3.42 Å) within each pair.

Strong intramolecular hydrogen bonding (H···Br 2.31 Å; O–H···Br 158°) as well as a complementary intermolecular hydrogen bonding pair (H–Br 2.43 Å; O–H···Br 175°) are also found in **5**. The tetranuclear [Ni₄(5-ehmp)₄(H₂O)₄Br₄] molecule is hydrogen bonded to four adjacent and symmetry related molecules through four complementary hydrogen bonding pairs (Fig. 7a). Each Ni₄ core can be treated as a tetrahedral node and an adamantane unit can therefore be generated which consists of ten Ni₄ units (Fig. 7b). This adamantane unit further extends in three directions to give a three dimensional structure which resembles the topology of diamond (Fig. 7c).

[Ni₄(5-ehmp)₄(μ-OAc)₂(OAc)₂(H₂O)₂] (6). Complex **6** crystallizes in the monoclinic space group $C2/c$ and its structure consists of a tetranuclear [Ni₄(5-ehmp)₄(μ-OAc)₂(OAc)₂(H₂O)₂] aggregate with a similar [Ni₄O₄] cubane core as found in **2** and **5**.
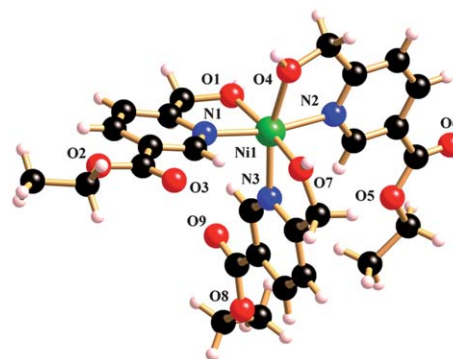

Fig. 5 Molecular structure of **4** with only one [Ni(5-ehmpH)₃]²⁺ dication being shown. Other moieties are omitted for clarity.
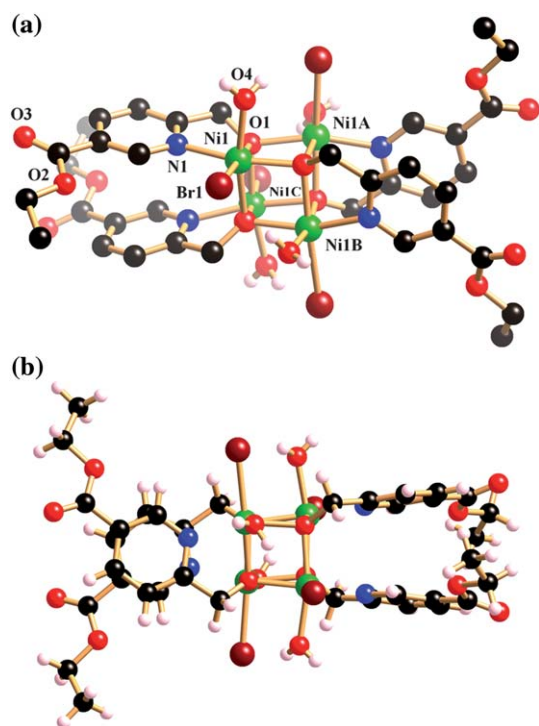
Fig. 6 Structure of **5** showing (a) a labelling scheme of selected atoms and (b) the perpendicular ligand pairs and staggered configuration.

However, it takes up a form that can be viewed as intermediate between **2** and **5**, with a mix of acetate and aqua supporting ligands, and a blend of bridging and unidentate acetates. The remaining two coordination sites of Ni(1) and Ni(1A) are therefore occupied by two oxygen atoms: one of each from bridging and monodentate acetate. Those of Ni(2) and Ni(2A) are also occupied by two oxygen atoms, but one from bridging acetate and the other from a coordinating H_2O ligand.

The different Ni (II) coordination spheres in **5** and **6** give rise to different arrangements of the 5-ehmp pairs. In **6**, the two 5-ehmp pairs are roughly coplanar (Fig. 8a) whereas in **5** they are orthogonal. The 5-ehmp pairs in **6** are staggered with a dihedral angle of 21.2° between six-member ring N1–C1–C2–C3–C4–C5 and N1A–C1A–C2A–C3A–C4A–C5A and 18.8° between six-member ring N2–C10–C11–C12–C13–C14 and N2A–C10A–C11A–C12A–C13A–C14A (Fig. 8b). Their ring-to-ring distances (3.96 and 4.09 Å) preclude effective π–π interactions.

Strong intramolecular (H–O 2.62 Å; O–H⋯O 172°) and intermolecular H-bonding interactions (H–O 2.67 Å; O–H⋯O 168°) are found in **6**. Each [Ni$_4$(5-ehmp)$_4$(μ-OAc)$_2$(OAc)$_2$(H$_2$O)$_2$] unit is hydrogen bonded to two adjacent symmetry equivalent unit through two complementary hydrogen bonded pairs, thereby forming a one dimensional chain structure in [1 0 1] direction (Fig. 9).

These reactions of 2-hydroxymethyl pyridine (hmpH) and 5-ethoxycarbonyl-2-hydroxymethylpyridine (5-ehmpH) with NiBr$_2$ and Ni(OAc)$_2$ give rise to a diverse range of products that are structurally distinctive to the extent that none of the isolated products have identical structures. They, however, share some common structural features. These hydroxymethylpyridines can coordinate as either chelating or bridging ligand. The native protonated form prefers to be chelating, thereby supporting
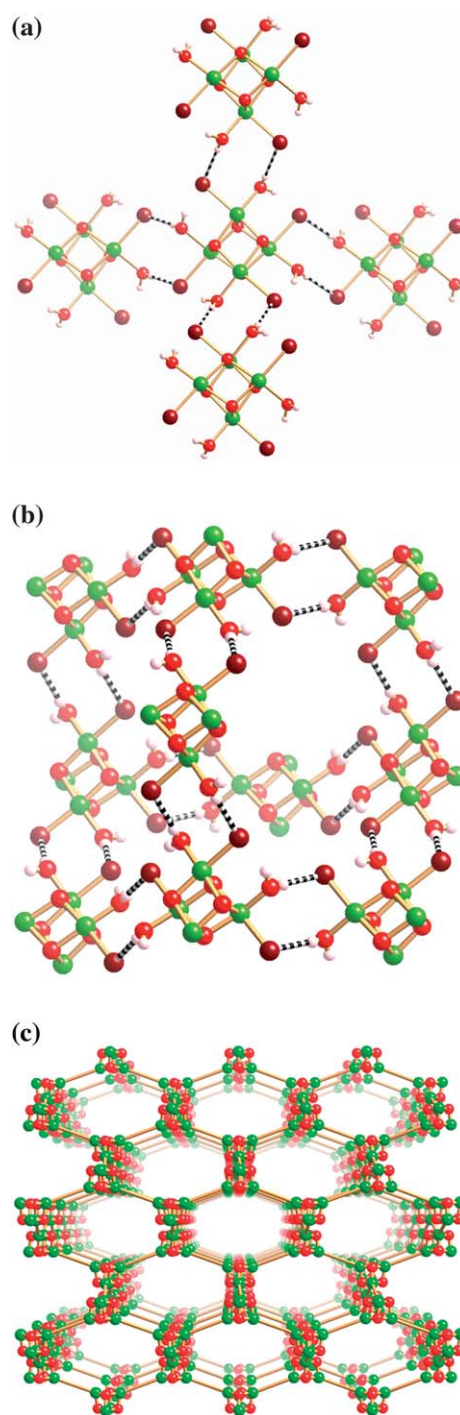

Fig. 7 Structure of **5** showing (a) a cluster is connected to four adjacent clusters through four complementary hydrogen bonding pairs, (b) an adamantine unit consists of ten cluster units and (c) three dimensional networks with a diamond topology; the hydrogen bond pairs were replaced by a single bond between the relevant Ni(II) atoms. All 5-ehmp ligands (a and b) and all 5-ehmp and Br, H$_2$O molecules are omitted for clarity.

mononuclear or dinuclear structure. Its deprotonated or conjugate base form is a stronger Lewis base, thereby serving as a bridging or capping ligand and supporting the formation of a cubane framework. Within the common cubane core, there are several variations, depending on the secondary ligands. For
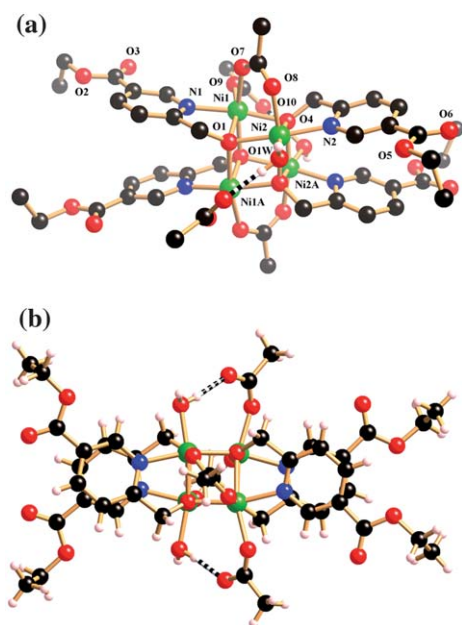
Fig. 8 Structure of **6**, (a) with labelling scheme and (b) showing the staggered conformation.
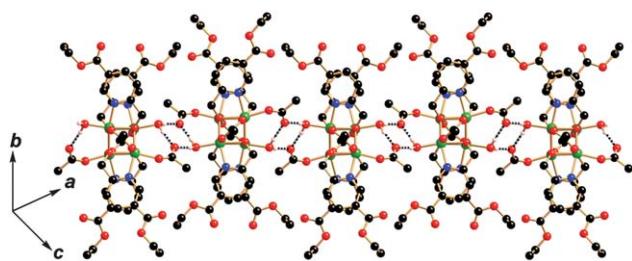

Fig. 9 Extended structure of **6** along the [1 0 1] direction.

example, acetate can be bridging or monodentate (*i.e.* terminal). Bromide and water can also be suitable terminal ligands. The cubane is further strengthened by intra- and intermolecular H-bonding between aqua and bromide or acetate ligands. The presence of an electron withdrawing substituent could also promote $\pi\cdots\pi$ interactions of the aromatic rings through reduction of electron density (comparing **2** and **5**). These cubanes are formed from deprotonation of the pyridyl alcohol ligand in the intermediate mono- or dinuclear forms. The resultant alkoxy oxygen atoms position as the corners of the Ni_4O_4 cubane by ideally serving as capping ligands of the system.

Acknowledgements

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