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Isolation of first row transition metal–carboxylate zwitterions†

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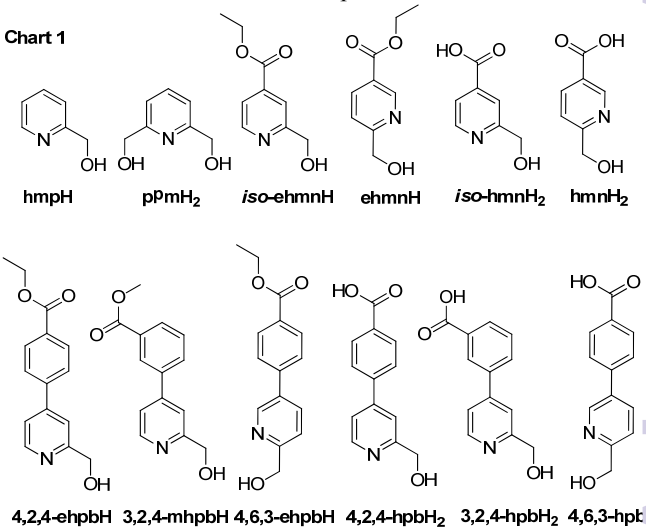
Zwitterionic 3*d* metal carboxylates of Zn(II), Cu(II), Ni(II) and Co(II) have been isolated and structurally authenticated by X-ray crystallography. A series of 2-hydroxymethylpyridine–carboxylate ligands with different size and shape demonstrate variable coordination modes with first row transition metals under different conditions, yielding a class of 17 complexes predominantly zwitterions. The nature of the ligands permits the carboxylates to be un-coordinated, anionic and conjugated, thereby balancing the positive charges on the metal centers.

Introduction

Zwitterions, or inner salts, are neutral molecules with opposite charges spatially separated in the same molecule.[1] Naturally occurring zwitterions are exemplified by the ubiquitous amino acids, $NH_3^+RCHCO_2^-$.[2] Synthetic metal–centered zwitterions, with metal ions as the positive charge center have been reported for the second and third row transition metals.[3] The polarity and solubility of these heavier metal centered zwitterions with borate, carbanion, sulfonate, sulfate and phosphate-based ligands are important for their roles in catalysis.[3a] The synthesis of first row transition metal based zwitterions, particularly metal–carboxylate zwitterions, is difficult because of the strong affinity of carboxylate anions for hard metal cations.[4] This hard acid–base interaction has led to a plethora of discrete metal–carboxylate clusters and, in the past 15 years, innumerable metal–organic frameworks (MOFs) assembled from first row transition metal ions and carboxylate-based organic ligands.[5]

Herein we report the synthesis of first row transition metal–carboxylate zwitterions by employing functionalized 2-hydroxymethylpyridine carboxylic acid or carboxylate ester ligands.[6] Examples of these ligands, ethyl 2-(hydroxymethyl)isonicotinate (*iso*-ehmnH) and ethyl 6-(hydroxymethyl)nicotinate (ehmnH) (Chart 1) were found to react with $Zn(NO_3)_2{\cdot}6H_2O$ to provide Zn–carboxylate zwitterions *trans*-$Zn(iso\text{-hmnH})_2(H_2O)_2$ (**1**) and *cis*-$Zn(hmnH)_2(H_2O)_2{\cdot}2H_2O$ (**2**) (*iso*-hmnH = 2-(hydroxymethyl)isonicotinate; hmnH = 2-(hydroxymethyl)nicotinate) which are intermediates in the formation of MOFs.[7] Complexes **1** and **2** are polar species that fluoresce blue and greenish-blue. To explore the diversity of these first row transition metal–carboxylate zwitterions and to better understand the relationship between the structure of the intermediates and the final MOFs, we have synthesized a series of hydroxymethylpyridine–carboxylic acids or hydroxymethylpyridine–carboxylate esters of different size and shape (Chart 1) as ligands for Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) salts. We have been able to isolate an array of 17 molecular species, predominantly zwitterions. In doing so, we have filled the literature gap in first row transition metal centered zwitterions and have devised a general strategy for the synthesis of zwitterionic coordination complexes.

Chart 1



Results and discussion

Reactions of $Zn(NO_3)_2·6H_2O$ with *iso*-ehmnH or ehmnH at 95 °C in DMF/H_2O (1:1, v/v) yielded colorless and greenish-orange solutions. Slow evaporation of these solutions at r.t. gave rise to zwitterionic complexes *trans*-[Zn(*iso*-hmnH)$_2$(H_2O)$_2$] (**1**) and *cis*-[Zn(hmnH)$_2$(H_2O)$_2$]·2H_2O (**2**).[7] Complex **1** and **2** are zwitterions with the positive charges from Zn^{2+} remotely neutralized by the two terminal carboxylates (Fig. 1). The octahedral Zn center is completed by a pair of chelating pyridine alcohol ligands and two coordinated water molecules. We propose zwitterions **1** and **2** are formed because hydroxymethylpyridine is a stronger chelator than the carboxylate under these conditions and results in overall charge neutrality. Notably, the isomeric ligands result in complexes of opposite stereochemistry, *viz trans* in **1** and *cis* in **2** (Fig. 1). The study of the crystal packing of **1** and **2** also revealed extensive hydrogen bonding interactions between coordinated water and hydroxyl as donors and free carboxylates as acceptors (Fig. S4, ESI†). These hydrogen bonding may also play a role in directing the configuration of the ligands.

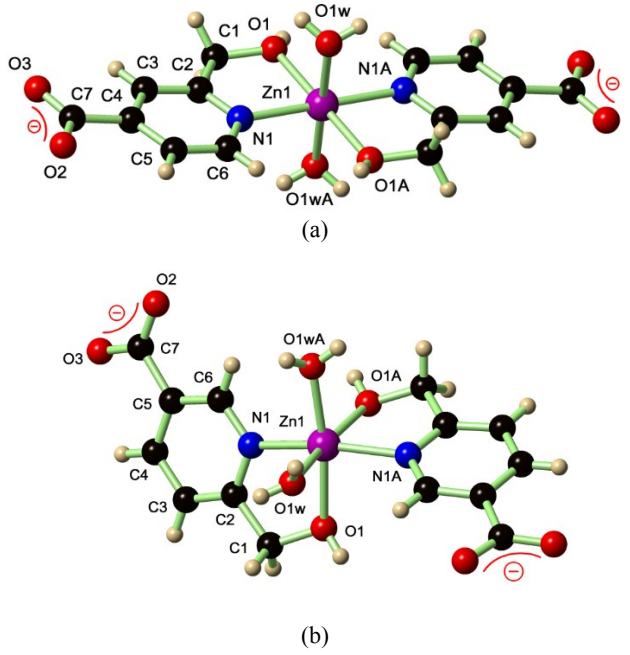


Fig. 1 Structure of *trans*-[Zn(*iso*-hmnH)$_2$(H_2O)$_2$] (**1**) (a) and *cis*-[Zn(hmnH)$_2$(H_2O)$_2$]·2H_2O (**2**) (b) with the dissociated H_2O molecules in **2** omitted. Symmetry codes for (**1**): A –*x*, –*y* + 1, –*z*; and (**2**): A –*x*, *y*, 0.5 – *z*. Selected C–O bond distances: C7–O2 1.248(2) Å, C7–O3 1.249(2) Å (**1**); C7–O2 1.234(2) Å, C7–O3 1.264(2) Å (**2**).

Other metals salts MX_2 (M = Co(II), Ni(II), Cu(II); X = NO_3, Cl) with *iso*-ehmnH and ehmnH resulted in amorphous, powdery products under similar conditions as those for complexes **1** and **2**. We therefore hydrolyzed *iso*-ehmnH and ehmnH to their respective acid forms *iso*-hmnH$_2$ and hmnH$_2$ (Chart 1). Reaction of *iso*-hmnH$_2$ and hmnH$_2$ with $Co(NO_3)_2·6H_2O$ or $Ni(NO_3)_2·6H_2O$ in DMF/H_2O/MeCN in the presence of trace amount of aqueous HNO_3 provided diffraction quality crystals of zwitterionic complexes *trans*-Co(*iso*-hmnH)$_2$(H_2O)$_2$ (**3**), *trans*-Ni(*iso*-hmnH)$_2$(H_2O)$_2$ (**4**) and *cis*-[Ni(hmnH)$_2$(H_2O)$_2$]·2H_2O (**5**) (Fig. S1, ESI†). Reaction of the corresponding metal chlorides, MCl_2 (M = Co, Ni, Zn) yielded the same zwitterionic complexes as determined by single-crystal X-ray diffraction.

The strong Jahn-Teller effect for Cu(II) (d^9) makes the reaction more susceptible to reaction variables such as ligand and metal sources, counterions, solvents, temperatures etc. It was not surprising, therefore, that we obtained different complexes (**6**–**11**) from reactions involving Cu(II) and *iso*-hmnH$_2$/hmnH$_2$ under different reaction conditions (Scheme 1).

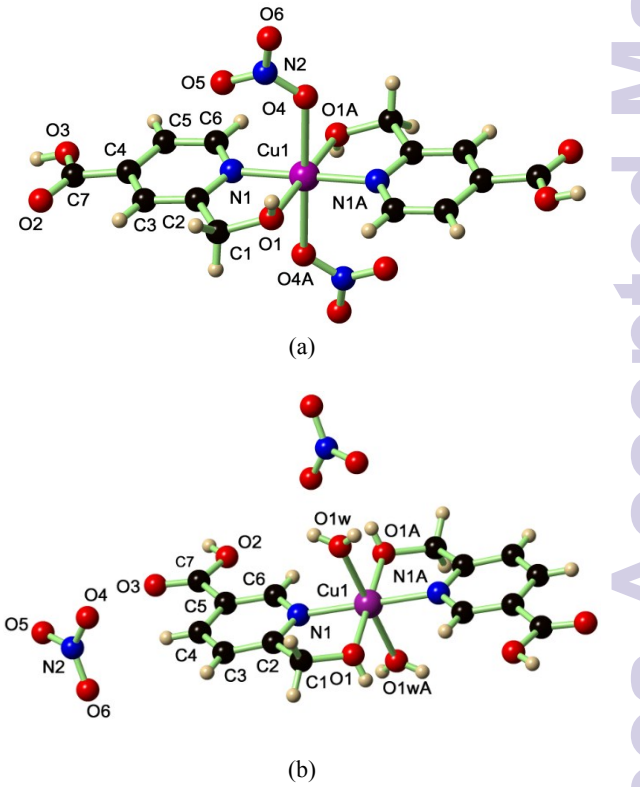
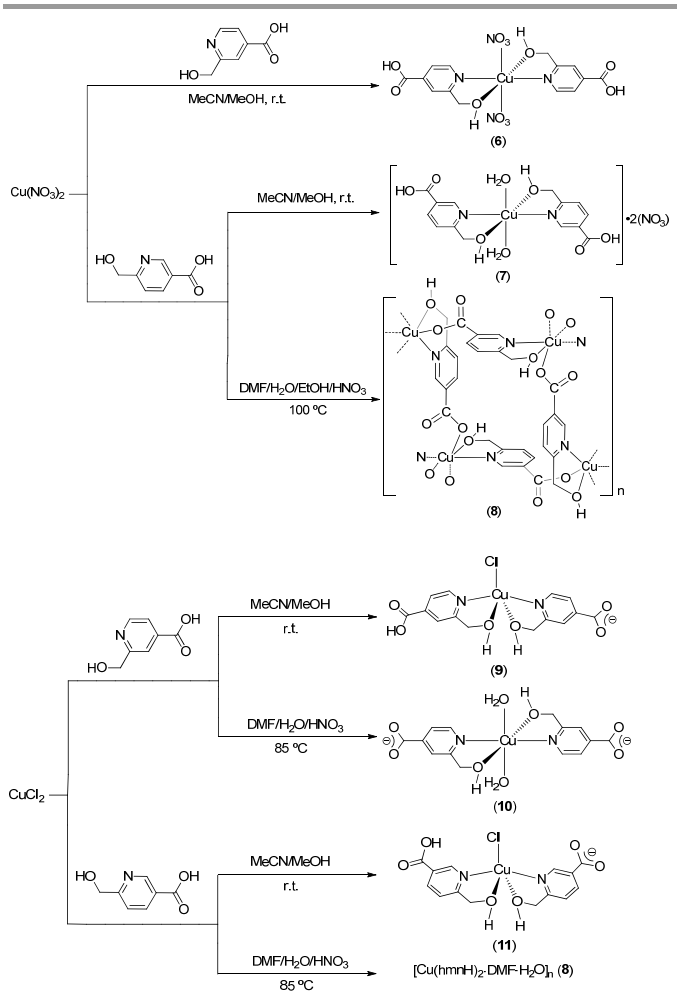


Fig. 2 Structures of *trans*-[Cu(*iso*-hmnH$_2$)$_2$(NO_3)$_2$]·2H_2O (**6**) (a) and *trans*-[Cu(hmnH$_2$)$_2$(H_2O)$_2$][NO_3]$_2$ (**7**) (b) with the dissociated H_2O molecules in **6** omitted. Symmetry codes for (**6**): A –*x*, –*y* + 1, –*z*; and (**7**): A –*x* + 1, *y* +1, – *z*. Selected C–O bond distances: C7–O2 1.213(5) Å, C7–O3 1.332(5) Å (**6**); C7–O2 1.324(4) Å, C7–O3 1.203(3) Å (**7**).

Reactions of $Cu(NO_3)_2·3H_2O$ with *iso*-hmnH$_2$ or hmnH$_2$ in MeCN/MeOH at r.t. provided non-zwitterionic, octahedral *trans*-[Cu(*iso*-hmnH$_2$)$_2$(NO_3)$_2$]·2H_2O (**6**) and *trans*-[Cu(hmnH$_2$)$_2$(H_2O)$_2$][NO_3]$_2$ (**7**) (Fig. 2). The ligands in both cases invariably prefer a *trans*-arrangement, and could accommodate different secondary coordination groups (NO_3 anion in **6** and H_2O in **7**).

When $CuCl_2·2H_2O$ was used as the metal source, zwitterionic, trigonal bipyramidal complexes [CuCl(*iso*-hmnH$_2$)(*iso*-

hmnH)]·H_2O (**9**) and $CuCl(hmnH_2)(hmnH)$ (**11**) were isolated in which the 2+ charge on Cu is balanced by one Cl and one carboxylate (Fig. 3a, 3c). The equatorial plane of the trigonal bipyramid is formed by the terminal Cl and two *cis* O atoms from the pyridine alcohol ligands while the apical positions are occupied by two *trans* located N atoms. By contrast, the reactions of $CuCl_2$ with *iso*-$hmnH_2$ in DMF/H_2O or DMF/H_2O/HNO_3 under solvothermal conditions resulted in the isolation of zwitterion *trans*-$Cu(iso\text{-}hmnH)_2(H_2O)_2$ (**10**) which is structurally analogous to complex **1** (Fig. 3b).



Scheme 1 Schematic presentation of the synthesis of complexes **6**–**11**.

The reaction of $hmnH_2$ with either $Cu(NO_3)_2{\cdot}3H_2O$ or $CuCl_2{\cdot}2H_2O$ under solvothermal conditions provided the same 2D, non-zwitterionic polymeric complex, $\{[Cu(hmnH)_2]{\cdot}DMF{\cdot}H_2O\}_n$ (**8**) (Scheme 1). The Cu(II) center is octahedral with the equatorial plane containing a pair of chelating N and O atoms from two *trans*-configuration hmnH ligands. The axial positions are occupied by two monodentate carboxylates. This results in an inter-connecting square-grid structure that is further stabilized by strong hydrogen bonding between the OH group of the pyridine alcohol moiety and the uncoordinated O atoms in the neighboring carboxylate ($O1\cdots O3^a$ 2.648(6) Å, $\angle O1{-}H\cdots O3^a$ 179(7)° ; *a*: $-0.5-x$, $0.5+y$, $1.5-z$) (Fig. 4a). The 2D network extends within the *bc* plane (Fig. 4b) and stack of these sheets along the *a* direction yields one dimensional channels wherein disordered DMF and H_2O solvents reside (Fig. 4c). Powder X-ray diffraction confirmed the phase purity of **8** (Fig. S2, ESI†). Thermogravimetric analysis indicated that the framework of **8** is stable till around 210 °C, after which decomposition follows accompanied by the loss of DMF solvates (Fig. S3, ESI†).

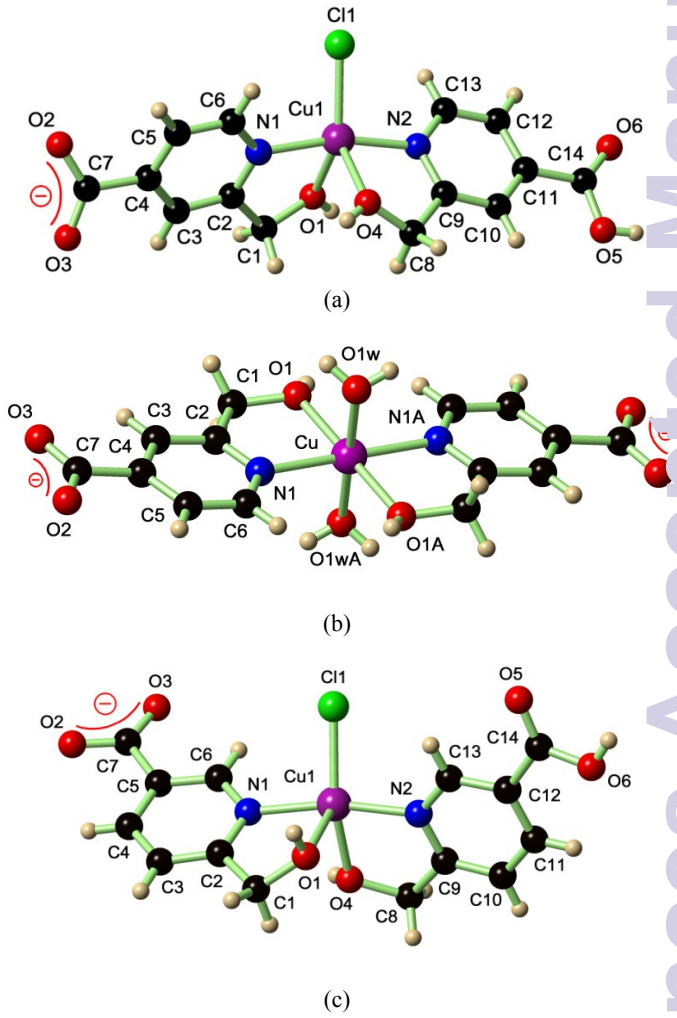


Fig. 3 Structures of $[CuCl(iso\text{-}hmnH_2)(iso\text{-}hmnH)]{\cdot}H_2O$ (**9**) (a), *trans*-$[Cu(iso\text{-}hmnH)_2(H_2O)_2]$ (**10**) (b) and $[CuCl(hmnH_2)(hmnH)]$ (**11**) (c) with the dissociated H_2O molecules in **9** omitted. Selected C–O bond distances: C7–O2 1.264(3) Å, C7–O3 1.237(3) Å, C14–O5 1.321(3) Å, C14–O6 1.206(3) Å (**9**); C7–O2 1.239(2) Å, C7–O3 1.260(2) Å (**10**); C7–O2 1.263(2) Å, C7–O3 1.241(2) Å, C14–O5 1.200(2) Å, C14–O6 1.315(2) Å (**11**).

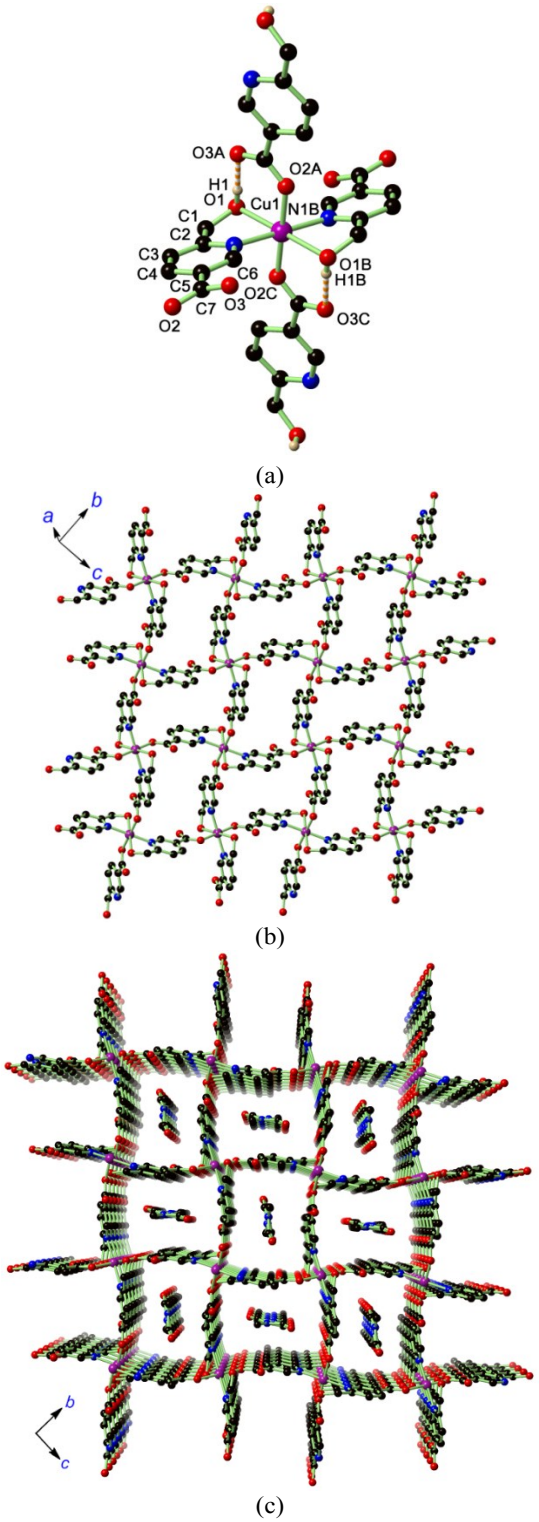
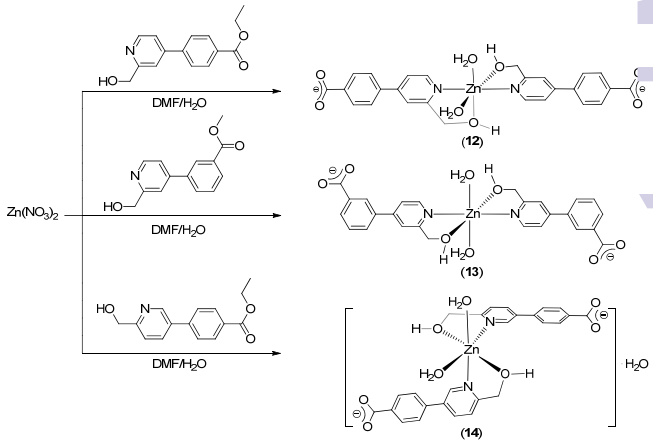


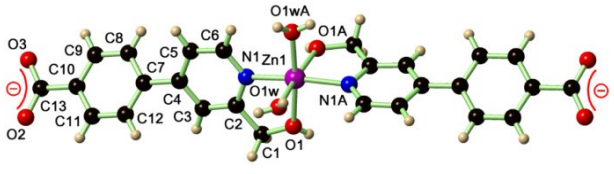
Fig. 4 Structure of $\{[Cu(hmnH)_2]\cdot DMF\cdot H_2O\}_n$ (**8**) showing, (a) coordination environment around Cu1, (b) 2D layer in *bc* plane and (c) stacking of the 2D layers to generate 1D channels along the *a* axis. Symmetry codes: A –0.5 – *x*, 0.5 + *y*, 1.5 – *z*; B –*x*, 1 – *y*, 2 – *z*; C 0.5 + *x*, 0.5 – *y*, 0.5 + *z*.

We extended the spacers and conjugation in these ligands by inserting a phenyl group between the ethyl carboxylate and pyridinemethanol, *viz*. 4,2,4-ehpbH, 3,2,4-mhpbH and 4,6,3-ehpbH (4,2,4-ehpbH = ethyl 4-(2-(hydroxymethyl)pyridin-4-yl)benzoate; 3,2,4-mhpbH = methyl 3-(2-(hydroxymethyl)pyridin-4-yl)benzoate; 4,6,3-ehpbH = ethyl 4-(6-(hydroxymethyl)pyridin-3-yl)benzoate) (Chart 1). Reaction of $Zn(NO_3)_2\cdot 6H_2O$ with 4,2,4-ehpbH, 3,2,4-mhpbH or 4,6,3-ehpbH in DMF/H_2O under solvothermal conditions gave rise to zwitterions *cis*-$Zn(4,2,4\text{-hpbH})_2(H_2O)_2$ (**12**), *trans*-$Zn(3,2,4\text{-hpbH})_2(H_2O)_2$ (**13**) and *cis*-$[Zn(4,6,3\text{-hpbH})_2(H_2O)_2]\cdot H_2O$ (**14**) (4,2,4-hpbH = 4-(2-(hydroxymethyl)pyridin-4-yl)benzoate; 3,2,4-hpbH = 3-(2-(hydroxymethyl)pyridin-4-yl)benzoate; 4,6,3-hpbH = 4-(6-(hydroxymethyl)pyridin-3-yl)benzoate) (Scheme 2). Similar reaction of 3,2,4-mhpbH with $Co(NO_3)_2\cdot 6H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$ yielded *trans*-$Co(3,2,4\text{-hpbH})_2(H_2O)_2$ (**15**) and *trans*-$Ni(3,2,4\text{-hpbH})_2(H_2O)_2$ (**16**) (Fig. S1, ESI†) which are isostructural with zinc analogue **13**. Reaction of 4,6,3-ehpbH with $Mn(NO_3)_2\cdot 4H_2O$ gave rise to a 2D polymer $[Mn(4,6,3\text{-hpbH})_2]_n$ (**17**).



Scheme 2 Schematic presentation of the synthesis of *cis*-$Zn(4,2,4\text{-hpbH})_2(H_2O)_2$ (**12**), *trans*-$Zn(3,2,4\text{-hpbH})_2(H_2O)_2$ (**13**) and *cis*-$[Zn(4,6,3\text{-hpbH})_2(H_2O)_2]\cdot H_2O$ (**14**).

There are some notable differences in the structures of complexes **12**–**16**. The structures of **12**, **13**, **15** and **16** mirror those of **2** and **1** (Scheme 2, Fig. 5a, 5b and Fig. S1, ESI†). However, the stereochemistry of *cis* **14** in which the two pyridine N atoms occupy equatorial and axial positions is in contrast to homologue *cis* **2** in which both pyridine N atoms are *trans* equatorial. Similarly, the *cis* stereochemistry of **12** and **14** is in contrast to the *trans* stereochemistry of **13**. The notable structural diversity among these zwitterions presumably suggests the varied σ-donor ability and, therefore, *trans* influence of the pyridine atom in their respective ligand.



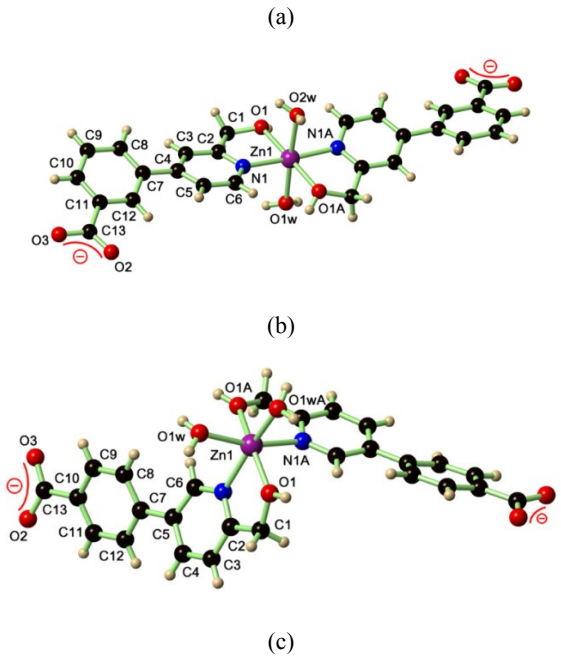


Fig. 5 Structures of *cis*-Zn(4,2,4-hpbH)$_2$(H$_2$O)$_2$ (**12**) (a), *trans*-Zn(3,2,4-hpbH)$_2$(H$_2$O)$_2$ (**13**) (b) and *cis*-Zn(4,6,3-hpbH)$_2$(H$_2$O)$_2$·H$_2$O (**14**) (c) with the dissociated H$_2$O molecules in **14** omitted for clarity. Symmetry codes for (**12**): A – *x*, *y*, 0.5 – *z;* (**13**): A – *x*, *y*, 0.5 – *z;* (**14**): A – *x* + 1, *y*, 0.5 – *z*. Selected C–O bond distances: C13–O2 1.251(5) Å, C13–O3 1.271(4) Å (**12**); C13–O2 1.239(2) Å, C13–O3 1.253(2) Å (**13**); C13–O2 1.268(2) Å, C13– O3 1.239(2) Å (**14**).

Although polymeric compound **17** has the same metal-to-ligand ratio as that of compound **8**, the coordination environments around each metal center are distinctively different. The pyridine alcohol pair chelating Mn in **17** resembles that found in **14**, where the N atoms are *cis* and O atoms *trans*. This disposition imposes the remaining sites, occupied by a pair of monodentate carboxylates, into a *cis* orientation (Fig. 6a). Each Mn(II) center connects to four adjacent centers through a pair of pyridine alcohol chelators and a pair of monodentate carboxylates to generate a two-dimensional layered structure in the *ac* plane (Fig. 6b). The different ligand arrangement in **17** relative to that of **8** also prevents hydrogen bonding between the alcoholic OH group and the proximate C=O group from the carboxylate on the same metal center. Instead, inter-layer hydrogen bonding (O1···O5^a 2.564(3) Å, ∠O1–H1O···O5^a 165(3)º; O4···O3^b 2.559(3) Å, ∠O4–H4O···O3^b 164(3)º; *a*: –*x* + 3, –*y*, –*z* + 2; *b*: –*x* + 2, –*y* + 1, –*z* + 4) is evident and the close stacking of adjacent layers block the apertures of the 2D layers, making **17** non-porous (Fig. S5, ESI†).

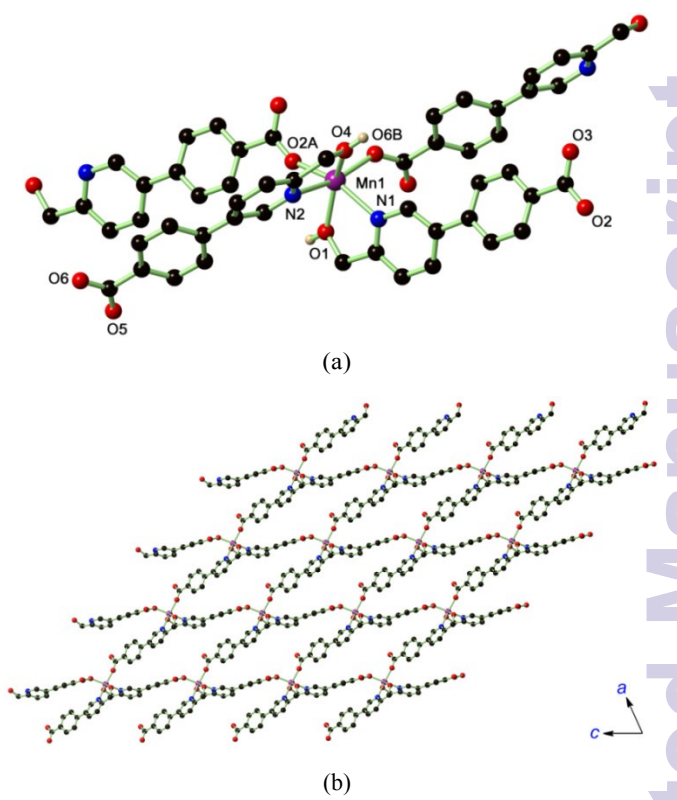


Fig. 6 Crystal structure of [Mn(4,6,3-hpbH)$_2$]$_n$ (**17**) showing, (a) the coordination environment around Mn1, and (b) the 2D layered structure in the *ac* plane. Hydrogen atoms except those on O4 and O1 in (a) are omitted.

Conclusions

Hydroxymethylpyridine–carboxylate (ester) ligands exhibit rich coordination chemistry by virtue of cooperative functionality that reacts differently under a diverse conditions of metal cations, solvents and temperatures, predominantly yielding unprecedented zwitterions of first row transition metals. This variable coordination behavior includes: I) both the hydroxymethylpyridine and carboxylic acid remaining protonated (**6** and **7**); II) hydroxymethylpyridine proton remains intact but the carboxylic acid is deprotonated to yield a zwitterion (**1**–**5**, **10**, **12**–**16**); III) admixture of types I and II (**9** and **11**); IV) the hydroxymethylpyridine proton remains intact and the carboxylic acid proton removed and bridges another metal center (**8** and **17**) and V) both the hydroxymethylpyridine proton and carboxylic acid protons are removed to form high dimensional MOFs. The reasons behind these structural and stereochemical outcomes may originate from the different σ-donor ability of the ligand or/and the rich hydrogen bonding interactions between coordinated water/alcoholic OH (donor) and free carboxylate (acceptor), and is one of the subjects of our future study. Zwitterion is a type of polar functionality, and including such function within MOFs may result MOFs with increased uptake capabilities towards gases such as CO$_2$. We are working towards s

these goals using pyridine alcohol ligands presented herein and their derivatives.

Experimental

All chemicals and solvents used were of A.R. grade and purchased from commercial suppliers. They were used without further purification unless otherwise specified. ^{1}H NMR spectra were recorded on a Bruker (400 MHz) NMR spectrometer 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 a Perkin Elmer 2000 FT-IR spectrometer using KBr pellet. Elemental analyses were performed on a Perkin–Elmer PE 2400 CHNS elemental analyzer. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 thermogravimetric analyzer at a heating rate of 10 °C/min under a nitrogen gas flow in an Al_2O_3 pan. Powder X-ray diffraction (PXRD) spectra were recorded with a Bruker D8 GADDS (General Area Detector Diffraction System) micro-diffractometer equipped with a VANTEC-2000 area detector with Φ rotation method. The X-ray generated from a sealed Cu tube was monochromated by a graphite crystal and collimated by a 0.5 mm MONOCAP (λ Cu-Kα = 1.54178 Å). The tube voltage and current were 40 kV and 40 mA, respectively.

Synthesis of ethyl 2-(hydroxymethyl)isonicotinate (*iso*-ehmnH) and ethyl 2-(hydroxymethyl)nicotinate (ehmnH)

Ethyl 2-(hydroxymethyl)isonicotinate (*iso*-ehmnH) and ethyl 2-(hydroxymethyl)nicotinate (ehmnH) were synthesized following the published procedure.[6a] Yield 50% for *iso*-ehmnH over two steps from pyridine-2,4-dicarboxylic acid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, J = 5.0 Hz, 1H), 7.86 (s, 1H), 7.77 (d, J = 4.9 Hz, 1H), 4.84 (s, 2H), 4.40 (q, J = 7.1 Hz, 2H), 3.59 (br, 1H), 1.40 (t, J = 7.1 Hz, 3H) ppm. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.3, 161.8, 149.6, 138.9, 121.8, 120.3, 64.8, 62.2, 14.5 ppm. MS (ESI, $CHCl_3$, 150 °C): 182.1 *m/z* : $[M+H]^+$. Anal. Calcd. (%) for $C_9H_{11}NO_3$: C 59.66, H 6.12, N 7.73; found: C 59.84, H 5.45, N 7.82. IR (KBr pellet): 3241 (br), 2988 (w), 2908 (w), 2830 (w), 1728 (s), 1607 (s), 1567 (s), 1479 (m), 1448 (m), 1398 (s), 1366 (m), 1299 (s), 1232 (m), 1204 (s), 1098 (s), 1063 (s), 1024 (s), 923 (w), 905 (w), 868 (m), 813 (w), 767 (s), 717 (m), 687 (s), 600 (w), 493 (w) cm^{-1}.

Yield 52% for ehmnH over two steps from pyridine-2,5-dicarboxylic acid. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.5, 164.0, 150.3, 138.1, 125.6, 120.3, 64.7, 61.8, 14.6 ppm. MS (ESI, $CHCl_3$, 150 °C): 182.3 *m/z*: $[M+H]^+$, 204.1 *m/z*: $[M+Na]^+$. Anal. Calcd. 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%. IR (KBr pellet): 3417 (sh), 3214 (s), 2986 (m), 2910 (m), 2840 (m), 2776 (w), 2704 (m), 2646 (w), 2574 (w), 2417 (w), 2262 (w), 2138 (w), 1992 (w), 1877 (w), 1860 (w), 1716 (s), 1659 (sh), 1626 (w), 1604 (s), 1575 (s), 1496 (w), 1476 (s), 1453 (s), 1399 (w), 1383 (s), 1366 (s), 1294 (s), 1272 (s), 1253 (s), 1216 (s), 1135 (s), 1110 (s), 1077 (s), 1027 (s), 878 (m), 859 (s), 812 (m), 785 (m), 761 (s), 722 (m), 694 (m), 667 (m), 643 (m), 561 (w), 476 (w), 457 (m), 422 (w), 407 (w) cm^{-1}.

Synthesis of 2-(hydroxymethyl)isonicotinic acid (*iso*-hmnH$_2$)

iso-EhmnH (4.84 g, 26.7 mmol) was dissolved in THF/H_2O (40 mL, *v*:*v* = 1:1). KOH (4.58 g, 81.6 mmol, 3 eq.) was added as solid and the mixture stirred at 100 °C for 20 h and then cooled to r.t. The mixture was further cooled in ice-water and then HNO_3 added to adjust the pH to 4–5. The solvent was removed under vacuum. The organic part in the solid mixture was then extracted twice with 400 mL of ethanol and the solvent removed. The powder contains inorganic material was added in hot *iso*-propanol and then filtered, evaporation of *iso*-propanol yielded *iso*-hmnH$_2$ as white powder. Yield 2.93 g, 72%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.61 (d, J = 5.0 Hz, 1H), 7.91 (s, 1H), 7.65 (d, J = 4.8 Hz, 1H), 4.62 (s, 2H), 4.42 (broad, 9H) ppm. ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): δ 167.6, 163.9, 150.1, 141.3, 121.8, 120.1, 64.9 ppm. MS (ESI, MeOH, 150 °C): 152.07 *m/z*: $[M–H]^-$. Anal. Calcd. (%) for $C_7H_7NO_3$: C 54.90, H 4.61, N 9.15; found: C 54.64, H 4.16, N 9.15. IR (KBr pellet): 3420 (s, br), 3048 (m, sh), 2939 (w), 2870 (w), 2642 (w), 1959 (w), 1667 (s), 1630 (s), 1618 (s), 1584 (s), 1546 (s), 1450 (m), 1413 (m), 1384 (s), 1334 (m), 1281 (w), 1252 (w), 1215 (w), 1117 (w), 1102 (w), 1061 (s), 1045 (s), 1027 (m), 985 (w), 974 (w), 946 (w), 905 (w), 879 (m), 788 (s), 773 (s), 731 (m), 697 (m), 681 (m), 661 (m), 627 (m), 569 (m), 500 (m), 421 (m) cm^{-1}.

Synthesis of 2-(hydroxymethyl)nicotinic acid (hmnH$_2$)

2-(Hydroxymethyl)nicotinic acid (hmnH$_2$) was prepared using the same method as *iso*-hmnH$_2$. Yield: approximately 75 %. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.95 (s, 1H), 8.20–8.23 (m, 1H), 7.50 (d, J = 8.0 Hz, 1H), 5.38 (br, 4H), 4.61 (s, 2H) ppm. ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): δ 167.4, 164.1, 149.5, 137.1, 129.5, 119.4, 64.2 ppm. MS (ESI, MeOH, 150 °C): 152.07 *m/z*: $[M–H]^-$. Anal. Calcd. (%) for $C_7H_7NO_3$: C 54.90, H 4.61, N 9.15; found: C 53.19, H 4.45, N 8.75. IR (KBr pellet): 3390 (s), 2914 (br), 2631 (w), 2524 (m), 2481 (m), 2450 (m), 2024 (w), 2001 (w), 1971 (w), 1935 (w), 1724 (s), 1641 (s), 1607 (s), 1542 (m), 1449 (s), 1396 (s), 1331 (m), 1315 (m), 1241 (m), 1134 (s), 1077 (s), 1026 (m), 1001 (m), 964 (w), 865 (s), 822 (s), 743 (s), 687 (m), 637 (s), 525 (m), 483 (m), 456 (m) cm^{-1}.

Synthesis of ethyl 4-(2-(hydroxymethyl)pyridin-4-yl)benzoate (4,2,4-ehpbH)

Step 1. Methyl 4-chloro-2-pyridinecarboxylate (0.86 g, 5.0 mmol), 4-(methoxycarbonyl)phenylboronic acid (1.30 g, 7.2 mmol) and K_3PO_4 (10.6 g, 50 mmol) were mixed in toluene (80 mL), and de-aerated using N_2. $PdCl_2$(dppf) (0.29 g, 0.36 mmol) was added, and the mixture stirred at 110 °C for 48h under N_2 atmosphere. The solution was evaporated to dryness under vacuum, extracted with $CHCl_3$ and then dried over $MgSO_4$. Subsequent column purification with EA/hexane (1:1, *v*:*v*) gave a white solid of methyl 4-(2-(methoxycarbonyl)pyridin-4-yl)benzoate. Yield: 1.20 g, 88% based on methyl 4-chloro-2-

pyridinecarboxylate. ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.82 (d, J = 4.8 Hz, 1H), 8.41 (s, 1H), 8.37 (s, 1H), 8.15 (d, J = 7.4 Hz, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.78 – 7.70 (m, 1H), 7.60 (m, 1H), 3.97 (s, 3H), 4.05 (s, 3H) ppm. ^{13}C {^{1}H} (101 MHz, $CDCl_3$): δ 166.9, 166.0, 150.8, 149.2, 149.0, 141.8, 131.5, 130.9, 127.5, 125.1, 123.5, 53.4, 52.7 ppm. MS (ESI, MeOH, 150 °C): 272.08 *m/z*: $[M+H]^+$. Anal. Calcd. for $C_{15}H_{13}NO_4$: C 66.41, H 4.83, N 5.16; found: C 66.44, H 4.31, N 5.15. IR (KBr pellet): 3417 (w), 3078 (w), 3042 (w), 3001 (w), 2952 (w), 2851 (w), 1955 (w), 1824 (w), 1729 (s), 1716 (s), 1600 (s), 1575 (w), 1543 (w), 1451 (m), 1441 (s), 1420 (w), 1397 (w), 1377 (w), 1321 (s), 1292 (s), 1251 (s), 1238 (m), 1195 (w), 1185 (w), 1133 (m), 1120 (s), 1105 (m), 1050 (m), 1016 (w), 997 (w), 914 (w), 874 (w), 847 (m), 830 (w), 788 (w), 767 (s), 721 (m), 708 (w), 700 (w), 656 (w), 583 (w), 528 (w), 499 (w), 477 (w), 435 (w), 407 (w) cm^{-1}.

Step 2. To a degassed EtOH (100 mL) solution containing methyl 4-(2-(methoxycarbonyl)pyridin-4-yl)benzoate (1.20 g, 4.4 mmol) and $NaBH_4$ (0.11 g, 3.0 mmol) was slowly added $CaCl_2$ (0.50 g, 4.42 mmol) at 0 °C with stirring. After the addition completed, the mixture was stirred for 3 h at the same temperature. The reaction was quenched by dropwise addition of concentrated H_2SO_4. The resultant mixture was evaporated to dryness under vacuum, extracted with $CHCl_3$, then dried over anhydrous $MgSO_4$. Removal of solvent followed by column purification with EA/hexane (3:1, *v:v*) gave a white solid of the transesterfication product ethyl 4-(2-(hydroxymethyl)pyridin-4-yl)benzoate. Yield: 0.90 g, 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, J = 5.1 Hz, 1H), 8.16 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.50 (s, 1H), 7.45 (d, J = 5.1 Hz, 1H), 4.85 (s, 2H), 4.42 (q, J = 7.1 Hz, 2H), 3.67 (s, 1H), 1.42 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5, 160.3, 149.6, 148.5, 142.7, 131.5, 130.7, 127.5, 121.0, 118.8, 64.8, 61.6, 14.7 ppm. MS (ESI, MeOH, 150 °C): 258.15 *m/z*: $[M+H]^+$. Anal. Calcd. for $C_{15}H_{15}NO_3$: C 70.02, H 5.88, N 5.44; found: C 70.23, H 5.55, N 5.28. IR (KBr pellet): 3428 (w), 3154 (w), 2983 (w), 2908 (w), 2844 (w), 2822 (w), 1713 (s), 1665 (w), 1636 (w), 1603 (s), 1577 (w), 1547 (w), 1480 (w), 1465 (w), 1444 (w), 1419 (w), 1398 (w), 1364 (w), 1315 (w), 1290 (m), 1276 (s), 1183 (w), 1126 (m), 1117 (m), 1105 (m), 1066 (m), 1048 (w), 1029 (w), 1018 (w), 1104 (w), 981 (w), 880 (w), 867 (w), 849 (w), 831 (m), 771 (s), 742 (w), 733 (w), 702 (w), 659 (w), 612 (w), 586 (w), 521 (w), 495 (w), 443 (w), 435 (w), 428 (w) cm^{-1}.

Synthesis of methyl 3-(2-(hydroxymethyl)pyridin-4-yl)benzoate (3,2,4-mhpbH)

Ligand 3,2,4-mhpbH was synthesized following the same route as described for 4,2,4-ehpbH.

Step 1. Methyl 3-(2-(methoxycarbonyl)pyridin-4-yl)benzoate was formed as a white solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 4.7 Hz, 1H), 8.41 (d, J = 1.2 Hz, 1H), 8.36 (s, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 3.3 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 4.04 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.8, 166.1, 150.8, 149.2, 149.1, 137.9, 131.7, 131.0, 129.8, 128.6, 125.0, 123.5, 53.4, 52.8 ppm. MS (ESI, MeOH, 150 °C): 272.11 *m/z*: $[M+H]^+$. Anal. Calcd. (%) for $C_{15}H_{13}NO_4$: C 66.41, H 4.83, N 5.16; found: C 66.66, H 4.28, N 5.11. IR (KBr pellet): 3410 (w), 3025 (w), 2958 (w), 1747 (m), 1716 (s), 1600 (m), 1589 (w), 1549 (w), 1508 (w), 1468 (w), 1439 (s), 1406 (w), 1329 (s), 1303 (s), 1277 (s), 1243 (s), 1185 (w), 1136 (w), 1109 (w), 1084 (w), 1059 (w), 1002 (w), 977 (w), 914 (w), 897 (w), 878 (w), 857 (w), 835 (w), 785 (m), 777 (w), 755 (s), 723 (m), 709 (w), 688 (w), 676 (w), 623 (w), 594 (w), 535 (w), 486 (w), 419 (w) cm^{-1}.

Step 2. Methyl 3-(2-(hydroxymethyl)pyridin-4-yl)benzoate was formed as a white solid in 80% yield. In situ transesterification was not observed. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 4.9 Hz, 1H), 8.30 (s, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.55 (m, 2H), 7.43 (d, J = 4.7 Hz, 1H), 4.84 (s, 2H), 3.95 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.9, 160.6, 149.6, 148.5, 138.8, 131.7, 130.5, 129.6, 128.6, 120.8, 118.8, 64.9, 52.7 ppm. MS (ESI, MeOH, 150 °C): 244.07 *m/z*: $[M+H]^+$. Anal. Calcd. (%) for $C_{14}H_{13}NO_3$: C 69.12, H 5.39, N 5.76; found: C 69.48, H 4.89, N 5.63. IR (KBr pellet): 3424 (w), 3146 (w), 3069 (w), 3039 (w), 2949 (w), 2919 (w), 2847 (w), 2637 (w), 2054 (w), 1982 (w), 1933 (w), 1888 (w), 1835 (w), 1768 (w), 1725 (s), 1612 (m), 1599 (m), 1585 (w), 1551 (w), 1493 (w), 1478 (w), 1438 (w), 1402 (m), 1362 (w), 1321 (m), 1309 (m), 1293 (m), 1258 (s), 1215 (w), 1203 (m), 1173 (w), 1113 (s), 1088 (m), 1067 (w), 1034 (s), 1005 (m), 980 (w), 966 (w), 916 (w), 898 (w), 864 (m), 834 (w), 824 (m), 774 (w), 758 (s), 698 (m), 678 (w), 664 (w), 628 (m), 580 (w), 545 (w), 500 (w), 465 (w), 422 (w) cm^{-1}.

Synthesis of ethyl 4-(6-(hydroxymethyl)pyridin-3-yl)benzoate (4,6,3-ehpbH)

Ligand 4,6,3-ehpbH was synthesized following the same route as described for 4,2,4-ehpbH.

Step 1. Methyl 4-(6-(methoxycarbonyl)pyridin-3-yl)benzoate was formed as a white solid in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (d, J = 1.8 Hz, 1H), 8.23 (d, J = 8.1 Hz, 1H), 8.18 (s, 1H), 8.16 (s, 1H), 8.06 (m, 1H), 7.71 (s, 1H), 7.68 (s, 1H), 4.04 (s, 3H), 3.96 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.9, 165.9, 148.7, 147.6, 141.4, 139.1, 135.8, 130.9, 127.8, 125.6, 53.4, 52.7 ppm. MS (ESI, MeOH, 150 °C): 271.99 *m/z*: $[M+H]^+$. Anal. Calcd. (%) for $C_{15}H_{13}NO_4$: C 66.41, H 4.83, N 5.16; found: C 66.49, H 4.97, N 5.15. IR (KBr pellet): 3418 (w), 2959 (w), 2919 (w), 2840 (w), 1720 (s), 1608 (w), 1589 (w), 1578 (w), 1558 (w), 1476 (w), 1449 (w), 1430 (s), 1418 (w), 1364 (w), 1317 (s), 1288 (s), 1273 (s), 1240 (s), 1190 (m), 1130 (m), 1124 (m), 1104 (s), 1033 (w), 1018 (w), 1001 (w), 950 (m), 875 (w), 851 (m), 828 (w), 799 (w), 767 (s), 701 (m), 683 (w), 644 (w), 628 (w), 522 (w), 521 (w), 486 (w), 411 (w) cm^{-1}.

Step 2. Transesterfication product ethyl 4-(6-(hydroxymethyl)pyridin-3-yl)benzoate was formed as a white solid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.16 (s, 1H), 8.14 (s, 1H), 7.92 (dd, J = 8.1, 2.1 Hz, 1H), 7.66 (s, 1H), 7.64 (s, 1H), 7.37 (d, J = 8.1 Hz, 1H), 4.83 (s, 2H), 4.41 (q, J = 7.1 Hz, 2H), 3.75 (s, 1H), 1.42 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 159.2, 147.5, 142.3, 135.7, 134.9, 130.7, 130.6, 127.4, 120.9, 64.6, 61.5, 14.7 ppm. MS (ESI, MeOH, 150 °C): 258.16 *m/z*: $[M+H]^+$. Anal. Calcd. for $C_{15}H_{15}NO_3$: C 70.02, H 5.88, N 5.44; found: C 69.70, H 5.16, N

5.29. IR (KBr pellet): 3413 (w), 3184 (m), 3059 (w), 3029 (w), 3007 (w), 2953 (w), 2896 (w), 2838 (w), 2708 (w), 2658 (w), 1717 (s), 1607 (m), 1576 (w), 1514 (w), 1481 (w), 1433 (m), 1418 (w), 1377 (m), 1364 (m), 1319 (w), 1290 (s), 1276 (s), 1210 (w), 1187 (m), 1103 (s), 1073 (s), 1023 (w), 1007 (s), 979 (w), 965 (w), 874 (w), 840 (m), 770 (s), 701 (s), 652 (w), 630 (w), 552 (w), 476 (w), 424 (w), 410 (w) cm^{-1}.

Synthesis of *trans*-[Zn(*iso*-hmnH)$_2$(H$_2$O)$_2$] (1)
Mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (30 mg, 0.1 mmol) and *iso*-ehmnH (36 mg, 0.2 mmol) were dissolved in DMF/H_2O (6 mL, *v*:*v* = 1:1) and the mixture heated at 95 °C for 72h to give a colorless solution which was filtered. Slow evaporation of the solution yielded colorless crystals of **1** which were collected, washed with H_2O and drying under vacuum. Yield: 25 mg, 62% based on Zn. MS (ESI, MeOH and trace DMF/H_2O, 150 °C): 369.7 *m/z*: $[M-2H_2O+H]^+$. Anal. Calcd. (%) for $C_{14}H_{16}N_2O_8Zn$: C 41.45, H 3.98, N 6.91; found: C 41.78, H 3.74, N 7.01. IR (KBr pellet): 3347 (m), 3054 (m), 2914 (m), 2841 (m), 2513 (m), 1956 (w), 1683 (s), 1602 (s), 1549 (s), 1454 (s), 1386 (s), 1289 (m), 1258 (m), 1218 (m), 1125 (m), 1103 (m), 1074 (s), 1027 (m), 1008 (w), 898 (m), 867 (m), 779 (s), 717 (m), 699 (s), 554 (w), 499 (w), 427 (w) cm^{-1}.

Synthesis of *cis*-[Zn(hmnH)$_2$(H$_2$O)$_2$]·2H$_2$O (2)
Complex **2** was synthesized from $Zn(NO_3)_2 \cdot 6H_2O$ and ehmnH using the same reaction conditions described for the synthesis of **1**. Yield: 29 mg, 66 % based on Zn. MS (ESI, MeOH and trace DMF/H_2O, 150 °C): 369.8 *m/z*: $[M-2H_2O+H]^+$. Anal. Calcd. (%) for $C_{14}H_{20}N_2O_{10}Zn \cdot 2H_2O$: C 41.45, H 3.98, N 6.91; found: C 41.33, H 4.05, N 6.89. IR (KBr pellet): 3403 (s), 3116 (s), 3077 (s), 2934 (m), 2857 (w), 2703 (w), 2444 (m), 2222 (m), 2004 (w), 1892 (w), 1778 (m), 1713 (w), 1614 (s), 1589 (s), 1558 (s), 1490 (s), 1446 (s), 1369 (s), 1340 (s), 1276 (s), 1259 (m), 1223 (m), 1154 (s), 1128 (m), 1078 (s), 1038 (s), 1004 (w), 939 (s), 877 (s), 866 (s), 848 (w), 800 (s), 772 (s), 719 (w), 687 (s), 653 (s), 544 (s), 496 (w), 477 (w), 444 (m), 421 (s) cm^{-1}.

Synthesis of *trans*-[Co(*iso*-hmnH)$_2$(H$_2$O)$_2$] (3)
$Co(NO_3)_2 \cdot 6H_2O$ (29 mg, 0.1 mmol) and *iso*-$hmnH_2$ (30 mg, 0.2 mmol) were dissolved in DMF/H_2O/MeCN (6 mL, *v*:*v*:*v* = 1:1:1) and 5 drops (*ca*. 0.25 mL) of 68 % HNO_3 added. The mixture was kept at 100 °C for 36 h to give a large amount of orange crystals which were collected and dried under vacuum. Yield: 34 mg, 85% based on Co. Anal. Calcd. (%) for $C_{14}H_{16}CoN_2O_8$: C 42.12, H 4.04, N 7.02; found: C 42.23, H 4.02, N 6.82. IR (KBr pellet): 3296 (s), 3069 (sh), 3052 (sh), 2841 (w), 2498 (s, br), 1669 (sh), 1598 (s), 1564 (s), 1456 (m), 1420 (s), 1387 (s), 1342 (m), 1289 (m), 1256 (m), 1218 (w), 1124 (w), 1103 (w), 1068 (s), 1023 (w), 1009 (w), 910 (w), 896 (m), 867 (w), 778 (s), 718 (m), 699 (s), 545 (w), 503 (w), 428 (m) cm^{-1}.

Synthesis of *trans*-[Ni(*iso*-hmnH)$_2$(H$_2$O)$_2$] (4)
Complex **4** was synthesized from $Ni(NO_3)_2 \cdot 6H_2O$ and *iso*-$hmnH_2$ using the same reaction conditions described for the synthesis of **3**. Yield: 78% based on Ni. Anal. Calcd. (%) for $C_{14}H_{16}N_2NiO_8$: C 42.15, H 4.04, N 7.02; found: C 42.45, H 3.88, N 7.03. IR (KBr pellet): 3303 (s), 3086 (sh), 3055 (sh), 2848 (w), 2507 (s, br), 1953 (w), 1794 (sh), 1599 (s), 1542 (s), 1456 (m), 1421 (s), 1387 (s), 1342 (m), 1289 (m), 1258 (m), 1220 (w), 1126 (w), 1105 (w), 1066 (s), 1027 (w), 1007 (w), 897 (w), 866 (w), 779 (s), 719 (m), 701 (s), 602 (w), 547 (w), 506 (w), 429 (m) cm^{-1}.

Synthesis of *cis*-[Ni(hmnH)$_2$(H$_2$O)$_2$]·2H$_2$O (5)
Complex **5** was synthesized from $Ni(NO_3)_2 \cdot 6H_2O$ and $hmnH_2$ using the same reaction conditions described for the synthesis of **3**. Yield: 28 mg, 64% based on Ni. Anal. Calcd. (%) for $C_{14}H_{20}N_2NiO_{10}$: C 39.47, H 4.50, N 6.58; found: C 39.47, H 4.82, N 6.45, corresponding to **5** – 0.5H_2O. IR (KBr pellet): 3538 (s), 3255 (s), 3077 (s), 3049 (s), 2919 (m), 2844 (w), 2510 (w), 2010 (w), 1903 (w), 1687 (w), 1620 (s), 1596 (s), 1558 (s), 1509 (w), 1482 (w), 1456 (w), 1396 (m), 1367 (s), 1338 (s), 1280 (s), 1255 (w), 1156 (m), 1136 (m), 1036 (s), 1006 (w), 952 (w), 870 (w), 867 (w), 779 (m), 718 (w), 688 (w), 658 (w), 632 (w), 546 (w), 474 (w), 426 (w) cm^{-1}.

Synthesis of *trans*-[Cu(*iso*-hmnH$_2$)$_2$(NO$_3$)$_2$]·2H$_2$O (6)
$Cu(NO_3)_2 \cdot 3H_2O$ (48 mg, 0.20 mmol) and *iso*-$hmnH_2$ (61 mg, 0.4 mmol) were dissolved in MeOH/MeCN (6 mL, *v*:*v* = 2:1). The mixture was briefly stirred at r.t. and the small amount of precipitate was filtered off. The filtrate was allowed to slowly evaporate to give green crystals of **6**. Yield: 42 mg, 40% based on Cu. MS (ESI, MeOH, 150 °C): 278.0 *m/z*: [Cu(*iso*-$hmnH_2$)$(NO_3)]^+$, 368.0 *m/z*: $[Cu(iso\text{-}hmnH_2)_2\text{–}H]^+$. Anal. Calcd. (%) for $C_{14}H_{18}CuN_4O_{14}$: C 31.73, H 3.42, N 10.57; found: C 37.07, H 3.91, N 8.97, roughly corresponding to *trans*-[Cu(*iso*-$hmnH_2)_2(NO_3)_2]\cdot 2H_2O$ – 2H_2O + 3MeOH (C 34.61, H 4.44, N 9.50). IR (KBr pellet): 3434 (br, s), 2839 (w), 2782 (w), 2642 (w), 2505 (w), 2422 (w), 1952 (w), 1731 (m), 1638 (s), 1615 (s), 1561 (m), 1476 (w), 1384 (s), 1281 (m), 1258 (m), 1211 (w), 1181 (w), 1123 (w), 1097 (w), 1076 (w), 1036 (w), 988 (w), 902 (w), 871 (w), 808 (w), 761 (m), 721 (m), 687 (m), 575 (w), 532 (w), 472 (w), 426 (w) cm^{-1}.

Synthesis of *trans*-[Cu(hmnH$_2$)$_2$(H$_2$O)$_2$][NO$_3$]$_2$ (7)
Complex **7** was synthesized from $Cu(NO_3)_2 \cdot 3H_2O$ and $hmnH_2$ using the same reaction conditions described for the synthesis of **6**. Yield: 15% based on Cu. MS (ESI, MeOH, 150 °C): 368.01 *m/z* $[Cu(hmnH_2)_2\text{–}H]^+$. Anal. Calcd. (%) for $C_{14}H_{18}CuN_4O_{14}$: C 31.73, H 3.42, N 10.57; found: C 34.23, H 3.24, N 10.41, corresponding to *trans*-$[Cu(hmnH_2)_2(H_2O)_2][NO_3]_2$ – 2H_2O (C 34.05, H 2.86, N 11.35). IR (KBr pellet): 3424 (sh), 3182 (s), 3058 (s), 2932 (sh), 2579 (w), 2426 (w), 2008 (w), 1874 (w), 1763 (w), 1725 (s), 1714 (s), 1619 (s), 1558 (w), 1498 (m), 1435 (sh), 1385 (s), 1280 (m), 1257 (m), 1226 (s), 1210 (s), 1129 (s), 1046 (s), 1034 (s), 980 (m), 941 (w), 870 (m), 844 (w), 825 (m), 775 (s), 761 (s), 696 (sw), 643 (m), 535 (w), 499 (w), 429 (w) cm^{-1}.

Synthesis of {[Cu(hmnH)$_2$]·DMF·H$_2$O}$_n$ (8)

$Cu(NO_3)_2·3H_2O$ (24 mg, 0.1 mmol) and $hmnH_2$ (30 mg, 0.2 mmol) were dissolved in DMF/H_2O/EtOH (6 mL, *v*:*v*:*v* = 1:1:1) and 5 drops of 68% HNO_3 added (*ca*. 0.25 mL). The mixture was kept at 100 °C for 36 h to give a light blue solution. Slow evaporation of the solution yielded light blue crystals of **8**, which were collected and dried under vacuum. Yield: 15 mg, 33% based on Cu. Anal. Calcd. (%) for $C_{17}H_{21}CuN_3O_8$: C 44.49, H 4.61, N 9.16; found: C 44.60, H 3.57, N 8.32, corresponding to $[Cu(hmnH)_2·0.5DMF·0.5H_2O]_n$ ($C_{15.5}H_{17}CuN_{2.5}O_7$: C 44.98, H 4.14, N 8.46). IR (KBr pellet): 3469 (m), 3077 (m), 3048 (m), 2949 (w), 2907 (w), 2805 (w), 2661 (w), 2514 (w), 2431 (w), 1891 (w), 1714 (m), 1671 (s), 1618 (s), 1602 (s), 1557 (s), 1498 (w), 1439 (w), 1391 (s), 1347 (s), 1282 (s), 1255 (w), 1235 (w), 1164 (m), 1135 (w), 1099 (w), 1063 (m), 1045 (s), 986 (w), 922 (w), 868 (m), 854 (m), 799 (m), 733 (s), 726 (w), 686 (w), 671 (w), 657 (m), 573 (w), 520 (m), 475 (w), 434 (m) cm^{-1}.

Synthesis of [CuCl (*iso*-$hmnH_2$)(*iso*-hmnH)]·H_2O (9)

$CuCl_2·2H_2O$ (17 mg, 0.1 mmol) and *iso*-$hmnH_2$ (30 mg, 0.2 mmol) were dissolved in MeOH/MeCN (12 mL, *v*:*v* = 2:1) and the solution was slowly evaporated at r.t. to give blue crystals of **9** which were collected and dried under vacuum. Yield: 35 mg, 82% based on Cu. Anal. Calcd. (%) for $C_{14}H_{15}ClCuN_2O_7$: C 39.82, H 3.58, N 6.63; found: C 39.82, H 4.32, N 6.57. IR (KBr pellet): 3520 (s), 3420 (s), 3095 (m), 3051 (m), 2971 (m), 2892 (m), 2779 (m), 2695 (m), 2632 (m), 2585 (m), 2541 (m), 1947 (w), 1921 (w), 1718 (m), 1621 (s), 1590 (s), 1568 (s), 1552 (s), 1491 (w), 1445 (m), 1382 (s), 1278 (s), 1248 (s), 1204 (s), 1116 (w), 1100 (w), 1063 (s), 1035 (m), 909 (w), 893 (w), 863 (w), 784 (m), 765 (s), 714 (w), 700 (s), 683 (s), 652 (w), 590 (w), 539 (w), 500 (w), 472 (m), 432 (m) cm^{-1}.

Synthesis of *trans*-Cu(*iso*-$hmnH)_2(H_2O)_2$ (10)

$CuCl_2·2H_2O$ (9 mg, 0.1 mmol) and *iso*-$hmnH_2$ (15 mg, 0.2 mmol) were dissolved in DMF/H_2O (6 mL, *v*:*v* = 1:1) and 5 drops of 68 % HNO_3 (*ca*. 0.25 mL) added. The mixture was kept at 85 °C for 72h to give olive green crystals of **10** which was collected and dried under vacuum. Yield: 22 mg, 55% based on Cu. Anal. Calcd. (%) for $C_{14}H_{16}CuN_2O_8$: C 41.64, H 3.99, N 6.94; found: C 41.10, H 3.65, N 7.00. IR (KBr pellet): 3385 (s), 3294 (s), 3130 (s), 3088 (s), 3050 (s), 2905 (m), 2838 (m), 2721 (m), 1952 (w), 1618 (s), 1554 (s), 1494 (w), 1451 (m), 1384 (s), 1296 (m), 1278 (m), 1259 (m), 1213 (w), 1125 (w), 1100 (w), 1076 (m), 1035 (w), 1006 (w), 972 (w), 911 (w), 898 (w), 866 (w), 790 (s), 782 (s), 699 (s), 661 (w), 581 (w), 544 (w), 503 (w), 487 (w), 434 (w) cm^{-1}.

Synthesis of CuCl($hmnH_2$)(hmnH) (11)

$CuCl_2·2H_2O$ (17 mg, 0.1 mmol) and $hmnH_2$ (30 mg, 0.2 mmol) were dissolved in MeOH/MeCN (12 mL, *v*:*v* = 2:1) and the solution was slowly evaporated at r.t. to give blue crystals of **11** which were collected and dried under vacuum. Yield: 25 mg, 62% based on Cu. Anal. Calcd. (%) for $C_{14}H_{13}ClN_2O_6Cu$: C 41.59, H 3.24, N 6.93; found: C 40.73, H 3.15, N 6.78. IR (KBr pellet): 3185 (m), 3062 (m), 2921 (m), 2770 (m), 2607 (m), 2533 (m), 2500 (m), 2004 (w), 1886 (w), 1708 (s), 1616 (s), 1586 (s), 1557 (s), 1499 (w), 1388 (s), 1375 (s), 1351 (w), 1331 (w), 1259 (s), 1229 (s), 1211 (m), 1153 (w), 1136 (s), 1046 (s), 1031 (s), 996 (w), 983 (w), 945 (w), 884 (w), 872 (m), 862 (m), 802 (s), 778 (s), 755 (m), 706 (w), 682 (w), 652 (w), 539 (m), 514 (w), 502 (w), 471 (w), 425 (w) cm^{-1}.

Synthesis of *cis*-Zn(4,2,4-hpbH)$_2(H_2O)_2$ (12)

$Zn(NO_3)_2·6H_2O$ (11.2 mg, 0.038 mmol) and 4,2,4-ehpbH (19.3 mg, 0.075 mmol) were dissolved in DEF/EtOH/H_2O (5 mL, *v*:*v*:*v* = 2:2:1) and transferred to a glass bottle with screw cap. The bottle was heated in a programmable oven smoothly from 25 ºC to 110 ºC within 4 h and at 110 ºC for 3 days, and then cooled to r.t.. The formed colorless crystals of **12** were collected by filtration, wash with DMF and dry under vacuum. Yield: 15 mg, 72% based on Zn. MS (ESI, MeOH and trace DEF, 150 °C): 325.61 *m/z*: $[Zn(4,2,4\text{-hpbH})+MeOH]^+$. Anal. Calcd. (%) for $C_{26}H_{24}N_2O_8Zn$: C 55.98, H 4.34, N 5.02; found: C 55.76, H 4.02, N 4.94. IR (KBr pellet): 3285 (w), 2974 (w), 2923 (w), 2831 (w), 2607 (w), 2567 (w), 1930 (w), 1676 (w), 1619 (s), 1601 (s), 1561 (s), 1542 (sh), 1509 (w), 1470 (w), 1410 (w), 1364 (s), 1334 (m), 1282 (m), 1250 (w), 1193 (w), 1176 (w), 1134 (w), 1097 (w), 1087 (m), 1049 (m), 1017 (w), 965 (w), 885 (w), 868 (w), 838 (m), 787 (s), 734 (w), 706 (w), 645 (w), 595 (w), 538 (w), 513 (w), 488 (w), 439 (w), 413 (w) cm^{-1}.

Synthesis of *trans*-Zn(3,2,4-hpbH)$_2(H_2O)_2$ (13)

Complex **13** was synthesized following the same route as described for **12**. Yield 47% (based on Zn) as colorless crystals. MS (ESI, MeOH and trace DEF, 150 °C): 325.56 *m/z*: $[Zn(3,2,4\text{-hpbH})+MeOH]^+$. Anal. Calcd. (%) for $C_{26}H_{24}N_2O_8Zn$: C 55.98, H 4.34, N 5.02; found: C 55.41, H 4.23, N 4.99. IR (KBr pellet): 3266 (br), 3059 (w), 2931 (w), 2641 (w), 2503 (w), 1620 (s), 1591 (s), 1546 (vs), 1471 (w), 1447 (m), 1380 (vs), 1313 (w), 1274 (m), 1197 (w), 1167 (w), 1123 (w), 1077 (m), 1052 (s), 1025 (m), 961 (w), 923 (w), 904 (w), 880 (w), 839 (m), 819 (w), 769 (s), 754 (m), 728 (w), 711 (w), 689 (w), 678 (s), 630 (m), 546 (w), 501 (m), 478 (w), 437 (w), 415 (w) cm^{-1}.

Synthesis of *cis*-Zn(4,6,3-hpbH)$_2(H_2O)_2$ (14)

Complex **14** was synthesized following the same route as described for **12.** Yield 62% (based on Zn) as colorless crystals. MS (ESI, MeOH and trace DEF, 150 °C): 325.60 *m/z*: $[Zn(4,6,3\text{-hpbH})+MeOH]^+$, 404.89 *m/z*: $[Zn(4,6,3\text{-hpbH})+NaCl+3H_2O]^+$. Anal. Calcd. (%) for $C_{26}H_{26}N_2O_9Zn$: C 54.23, H 4.55, N 4.86; found: C 53.68, H 4.23, N 4.78. IR (KBr pellet): 3436 (br), 3103 (w), 3071 (w), 3037 (w), 2932 (w), 2906 (w), 2865 (w), 2725 (w), 2426 (w), 1950 (w), 1630 (w), 1609 (w), 1588 (m), 1566 (w), 1533 (m), 1489 (w), 1447 (w), 1415 (m), 1385 (s), 1369 (sh), 1317 (w), 1301 (w), 1243 (w), 1215 (w), 1183 (w), 1138 (w), 1108 (w), 1062 (w), 1046 (m), 1025 (w), 1010 (w), 990 (w), 948 (w), 871 (w), 832 (w), 819 (w), 790 (s), 744 (w), 731 (w), 72[illegible] (w), 706 (w), 668 (w), 649 (w), 566 (w), 551 (w), 525 (w), 496 (w), 448 (w), 438 (w), 418 (w) cm^{-1}.

Synthesis of *trans*-Co(3,2,4-hpbH)$_2(H_2O)_2$ (15)

$Co(NO_3)_2·6H_2O$ (3.6 mg, 0.013 mmol) and 3,2,4-mhpbH (6.0 mg, 0.025 mmol) were dissolved in DMF/EtOH/H_2O (9 mL, *v*:*v*:*v* = 4:4:1) and transferred to a 50 mL glass reactor with screw cap. The bottle was transferred to a programmable oven and heated smoothly from 25 ºC to 110 ºC within 4 h and at 130 ºC for 3 days before cooling to r.t. within 1.5 days to provide light orange crystals of **15**. Yield 6 mg, 51% (based on Co). Anal. Calcd. (%) for $C_{26}H_{24}CoN_2O_8·0.5H_2O$: C 55.72, H 4.50, N 5.00; found: C 55.40, H 4.32, N 5.00. IR (KBr pellet): 3234 (br), 3062 (s), 2925 (m), 2852 (m), 2641 (m), 2597 (m), 2509 (br), 1958 (w), 1921 (w), 1619 (vs), 1591 (vs), 1565 (vs), 1545 (vs), 1474 (w), 1450 (m), 1398 (vs), 1378 (vs), 1312 (m), 1286 (m), 1273 (m), 1200 (w), 1169 (w), 1122 (w), 1087 (w), 1073 (w), 1050 (vs), 1022 (m), 961 (w), 922 (w), 880 (m), 839 (m), 820 (m), 770 (vs), 754 (s), 732 (w), 690 (m), 679 (s), 629 (m), 592 (w), 549 (w), 502 (w), 484 (w), 437 (w), 418 (w) cm^{-1}.

Synthesis of ***trans*-Ni(3,2,4-hpbH)$_2$(H$_2$O)$_2$ (16)**

Complex **16** was synthesized following the same route as described for **15** from $Ni(NO_3)_2·6H_2O$ and 3,2,4-mhpbH. Yield 41.6 % based on Ni. Anal. Calcd. (%) for $C_{26}H_{24}N_2NiO_8·H_2O$: C 54.86, H 4.60, N 4.92; found: C 54.78, H 4.36, N 4.81. IR (KBr pellet): 3275 (br), 3059 (w), 2924 (m), 2852 (w), 2503 (br), 1745 (w), 1621 (s), 1591 (m), 1565 (m), 1542 (vs), 1504 (w), 1476 (w), 1448 (m), 1440 (s), 1380 (vs), 1338 (w), 1313 (w), 1286 (w), 1274 (w), 1202 (w), 1167 (w), 1123 (w), 1087 (w), 1049 (s), 1026 (m), 963 (w), 921 (w), 901 (w), 880 (w), 840 (w), 820 (w), 770 (s), 755 (m), 730 (w), 689 (m), 679 (m), 631 (m), 549 (w), 503 (w), 481 (w), 459 (w), 439 (w) cm^{-1}.

Synthesis of [Mn(4,6,3-hpbH)$_2$]$_n$ (17)

$Mn(NO_3)_2·4H_2O$ (2.51 mg, 0.01 mmol) and 4,6,3-ehpbH (5.14 mg, 0.02 mmol) were dissolved in DMF/EtOH/H_2O (4 mL, *v*:*v*:*v* = 2:1:1). The solution was then placed in a 50 mL glass reactor with screw cap in a programmable oven and heated smoothly from r.t. to 110 ºC and kept at 110 ºC for 3 days before cooling to r.t. during one and half days to provide colorless crystals of **17**. Yield: 2 mg, 39.1% based on Mn. Anal. Calcd. (%) for $C_{26}H_{20}MnN_2O_6·H_2O$: C 58.99, H 4.19, N 5.29; found: C 58.45, H 4.07, N 5.48. IR (KBr pellet): 3430 (br), 3057 (w), 2927 (w), 2887 (w), 2825 (w), 2821 (w), 2579 (br), 1606 (vs), 1593 (vs), 1570 (s), 1548 (s), 1519 (m), 1455 (s), 1388 (vs), 1308 (w), 1279 (w), 1235 (w), 1224 (w), 1183 (w), 1141 (w), 1105 (w), 1066 (s), 1042 (m), 1009 (m), 969 (w), 941 (w), 930 (w), 872 (w), 833 (w), 814 (w), 781 (s), 738 (w), 719 (w), 705 (m), 656 (m), 548 (m), 527 (m), 485 (w), 429 (w), 417 (w) cm^{-1}.

X-ray Crystallography

Crystallographic measurements (except **12**) were made on a Bruker AXS APEX II diffractometer by using graphite-monochromated Mo Kα (λ = 0.71073 Å) in the Institute of Materials Research and Engineering. Complex **12** was measured on an Agilent Technologies SuperNova Dual diffractometer with Cu Kα (λ = 1.54178 Å) X-ray Source in University of Malaya. The data were subjected for empirical absorption correction using SADABS[8] (except **12**) or spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm (**12**). All crystal structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with SHELXTL–97 program.[9]

For **8**, the DMF solvate adopts a symmetry induced disorder and the symmetry was suppressed using PART −1 instruction with the occupancy factors further fixed at 0.50. For **14**, the dissociated water molecule is disordered by symmetry and PART −1 was used to suppress the symmetry and the occupancy factors were further fixed at 0.50. All the H atoms on the OH, H_2O and/or –COOH groups were found for the difference Fourier map with O–H distances restrained to 0.83 Å while their thermal parameter fixed to $U_{iso}(H) = 1.2U_{eq}(O)$. A summary of the key crystallographic data for **1**–**17** are listed in Table 1.

Table 1 Summary of Crystallographic Data for **1**–**17**.

Compounds	**1**	**2**	**3**	**4**
formula	$C_{14}H_{16}N_2O_8Zn$	$C_{14}H_{20}N_2O_{10}Zn$	$C_{14}H_{16}CoN_2O_8$	$C_{14}H_{16}N_2NiO_8$
FW	405.66	441.69	399.22	399.00
crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
space group	*Pbca*	*C*2/*c*	*Pbca*	*Pbca*
a (Å)	7.0534(4)	13.6211(6)	7.1867(3)	7.1353(4)
b (Å)	13.3638(8)	7.7315(4)	13.3223(6)	13.2866(8)
c (Å)	16.8646(10)	16.8791(8)	16.8797(7)	16.8095(10)
α (°)	90.00	90.00	90.00	90.00
β (°)	90.00	103.7790(10)	90.00	90.00
γ (°)	90.00	90.00	90.00	90.00
V (Å^3)	1589.66(16)	1726.41(14)	1616.12(12)	1593.61(16)
Z	4	4	4	4
ρ_{calc} (g cm^{-3})	1.695	1.699	1.641	1.663
F(000)	832	912	820	824
μ (mm^{-1})	1.593	1.482	1.109	1.265
total reflns.	20767	15177	33694	45407
uniq. reflns.	1828	2152	4334	5008
obsd. reflns.	1528	1944	3448	3552
R_{int}	0.0336	0.0211	0.0231	0.0309
variables	124	138	125	124
R_1[a]	0.0233	0.0234	0.0358	0.0323
wR_2[b]	0.0659	0.0601	0.1059	0.0951
GOF[c]	1.087	1.085	1.114	1.045
ρ_{max}/ρ_{min}(e Å^{-3})	0.374/–0.301	0.376/–0.255	0.588/–0.533	0.603/–0.496

Table 1 Continued

5	**6**	**7**	**8**	**9**
$C_{14}H_{20}N_2NiO_{10}$	$C_{14}H_{18}CuN_4O_{14}$	$C_{14}H_{18}CuN_4O_{14}$	$C_{17}H_{21}CuN_3O_8$	$C_{14}H_{15}ClCuN_2O_7$
435.03	529.86	529.86	458.91	422.27
Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
*C*2/*c*	$P2_1/n$	*P*–1	$P2_1/n$	*P*–1
13.3910(4)	8.5580(4)	7.256(6)	7.451(2)	7.7474(7)
7.7123(2)	10.3042(5)	7.425(6)	10.916(3)	9.0283(8)
16.9892(5)	12.2558(6)	9.897	12.454(4)	11.6264(10)
90.00	90.00	89.716(17)	90.00	81.603(2)
104.4560(10)	108.0080(10)	77.622(17)	106.955(6)	80.274(2)
90.00	90.00	86.150(19)	90.00	81.512(2)
1699.02(8)	1027.81(9)	519.6(7)	968.9(5)	786.61(12)
4	2	1	2	2
1.701	1.712	1.693	1.573	1.783
904	542	271	474	430
1.203	1.145	1.133	1.178	1.601
22722	14171	12033	15551	11032
3736	2456	2115	2231	2852
3266	2262	1954	1435	2564
0.0246	0.0182	0.0625	0.0983	0.0278
138	163	163	163	241
0.0277	0.0527	0.0350	0.0719	0.0279
0.0746	0.1470	0.0946	0.2294	0.0758
1.046	1.055	1.136	1.089	1.063
0.484/–0.269	2.473/–0.786	0.518/–0.759	1.705/–1.186	0.538/–0.514

Table 1 Continued

10	**11**	**12**	**13**
$C_{14}H_{16}CuN_2O_8$	$C_{14}H_{13}ClCuN_2O_6$	$C_{26}H_{24}N_2O_8Zn$	$C_{26}H_{24}N_2O_8Zn$
403.83	404.25	557.84	557.84
Orthorhombic	Triclinic	Monoclinic	Monoclinic
Pbca	*P*–1	*C*2/*c*	*C*2/*c*
6.9918(5)	7.5935(3)	28.325(2)	25.0244(9)
13.1602(9)	7.7855(4)	7.1216(6)	7.5228(3)
17.1546(12)	14.6720(7)	12.6168(13)	12.9729(5)
90.00	83.0350(10)	90.00	90.00
90.00	86.3830(10)	114.533(14)	107.7859(7)
90.00	61.4210(10)	90.00	90.00
1578.45(19)	756.08(6)	2315.3(4)	2325.47(15)
4	2	4	4
1.699	1.776	1.600	1.593
828	410	1152	1152
1.432	1.656	1.973	1.113
15498	33421	7792	10557
1805	4605	2402	2666
1501	4255	1991	2433
0.0296	0.0204	0.0929	0.0181
124	226	180	178
0.0247	0.0242	0.0572	0.0289
0.0651	0.0663	0.1594	0.0790
1.019	1.045	1.060	1.047
0.404/–0.336	0.449/–0.370	0.909/–0.959	0.483/–0.419

Table 1 Continued

14	**15**	**16**	**17**
$C_{26}H_{26}N_2O_9Zn$	$C_{26}H_{24}CoN_2O_8$	$C_{26}H_{24}N_2NiO_8$	$C_{26}H_{20}MnN_2O_6$
575.86	551.40	551.18	511.38
Monoclinic	Monoclinic	Monoclinic	Triclinic
*C*2/*c*	*C*2/*c*	*C*2/*c*	*P*–*1*
26.264(2)	25.051(11)	24.917(4)	9.904(2)
8.4871(8)	7.425(3)	7.3870(11)	10.165(2)
12.0334(11)	12.951(6)	12.944(2)	2.286(3)
90.00	90.00	90.00	77.470(3)
114.801(2)	107.721(8)	107.482(4)	68.167(3)
90.00	90.00	90.00	85.302(3)
2434.9(4)	2294.8(16)	2272.6(6)	1120.9(4)
4	4	4	2
1.571	1.596	1.611	1.515
1192	1140	1144	526
1.069	0.806	0.912	0.636
7396	15227	11008	20302
2777	2637	2071	4246
2542	1495	1239	3197
0.0143	0.1697	0.1516	0.0544
192	178	178	322
0.0283	0.0575	0.0563	0.0410
0.0857	0.1167	0.1290	0.1069
1.043	0.988	1.009	1.017
0.414/–0.412	0.408/–0.437	0.482/–0.446	0.352/–0.377

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

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