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Centric and Acentric Networks Using Low-Symmetry Heterotopic Carboxylate/Pyridyl Ligands

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Four isomeric, heterotopic ligands, containing both a pyridyl and a carboxylate functional group, have been incorporated into a series of 1D and 2D coordination polymers with the low symmetry of the ligands postulated to aid the formation of acentric materials. The ligands contain pyridyl and benzoate functionalities separated by a hydrazinyl core, with the substitution positions on the two aromatic groups being either *meta* or *para* (yielding a total of 4 isomers). The neutral organic molecules have been structurally characterised and form hydrogen-bonding networks through interactions between the carboxylic acid, the pyridyl nitrogen atom and the hydrazinyl NH group, including an unusual acentric structure in which Z'=6 in the case of the 3-pyridyl/4-benzoic acid isomer (**3py4bzH**). Reactions with transition metal salts forms coordination polymers with the generic solvent-free formula $[ML_2]_n$ in all cases. The mixed meta/para substituted ligands (**3py4bzH** and **4py3bzH**) both form centrosymmetric coordination polymers, 1D and 2D respectively, containing similar M_2L_2 ring motifs due to the comparable angle between the coordinating groups in the two ligands. **3py3bzH** and **4py4bzH** both form acentric 4,4 sheets that pack in a helical manner with 4-fold and 3-fold screw axes, respectively, induced by the differences in geometry within the sheets.

Introduction

The rational design and synthesis of coordination polymers has been an increasingly active research field since its founding concepts were laid out by Hoskins and Robson over 25 years ago.[1] At the heart of research interests in this area, and in the broader area of crystal engineering, is the motivation to predictably generate new materials with the desired structural features 'programmed' into the components used in the self-assembly process.[2] The area has expanded to touch upon many disperate applications that exploit the physical and/or chemical properties of this class of materials.[3]

Chiral coordination polymers present a particular synthetic challenge, although they are of great potential benefit for enantioselective applications such as catalysis, separations and non-linear optical behaviour.[4] The most reliable route to chiral materials is through the inclusion of organic stereocentres or axial chirality in the ligands that are employed. However, there are many coordination networks that crystallise in chiral space groups with no intrinsic chirality in the system, so-called 'spontaneous resolution' which by common usage refers to chiral coordination frameworks forming from achiral components with both enantiomeric forms generated simultaneously.[5] Obtaining enantiopure materials rather than racemic mixtures from these chiral assembly processes has been attempted in numerous ways including by using induction agents,[6] seeding,[7] or even by the use of circularly polarized laser irradiation.[8]

Whilst there exists the potential for almost any species to crystallise in chiral space groups, the use of low symmetry ligands in coordination assemblies has been demonstrated by Lin and Evans to be more likely to lead to chiral materials.[9]

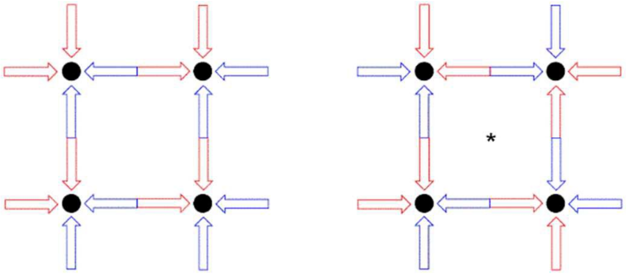

Figure 1: Heterotopic ligands can form either acentric (left) or centrosymmetric (right, * = inversion centre) networks, exemplified above by a (4,4) sheet.

The use of the short, ditopic carboxylate/pyridyl ligand nicotinate and longer analogues, such as pyridylethenylbenzoate and pyridylbenzoate, can give rise to chiral materials in which transition metal ions adopt a $(CO_2)_2(py)_2$ coordination environment (typically with an octahedral coordination geometry) to give rise to four-connected toplogies, *i.e.* (4,4) sheets and diamondoid nets (Figure 1).[10] The combination of carboxylate and pyridyl functionalities is pervasive in coordination polymers, typically

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Electronic Supplementary Information (ESI) available: PXRD data, additional diagrams, crystallographic refinement information/data. See DOI: 10.1039/x0xx00000x through the use of a mixture of dipyridyl and dicarboxylate ligands, and commonly has the advantage of excluding solvent from the inner coordination sphere and hence removing a source of structural unpredictablity.

In an effort to explore the wider applicability of this synthetic method, a ligand system with different substitutional isomers was designed. Herein we report coordination polymers synthesised using four isomeric carboxylate/pyridyl ligands with a hydrazinyl core which also provides a hydrogen bond donor group. The three atom link between the pyridyl and benzoic acid groups generates different ligand geometries to previous reported heterotopic ligands and results demonstrate that not only acentric structures can be obtained with ligands of this type.

Experimental Details

Synthetic Procedures

All starting materials and solvents were procured from standard commercial suppliers and were used without additional purification. NMR spectra were collected using a Bruker Avance 400 spectrometer operating at 400 MHz (^{1}H) or 100 MHz (^{13}C). Elemental analyses were conducted at the Campbell Analytical Laboratories, University of Otago, New Zealand or London Metropolitan University, UK. For all coordination polymers, powder X-ray diffraction was used to confirm bulk phase purity (see Supporting Information). PXRD spectra were obtained at room temperature using a Bruker X8 diffractometer equipped with Cu-Kα radiation (1.5418 Å).

Synthesis of Ligands

3py3bzH: 3-hydrazinobenzoic acid (0.609 g, 4 mmol) was suspended in acetonitrile (50 mL). 3-acetylpyridine (0.55 mL, 5 mmol) was added into the suspension. The reaction mixture was placed under reflux conditions overnight. A pale orange precipitate was recovered by vacuum filtration. Yield 0.811 g (79%). m.p. 261-262 °C. Found C, 65.24; H, 5.20; N, 16.12%; $C_{14}H_{13}N_3O_2$ requires C, 65.19; H, 5.20; 16.29%. ^{1}H(400 MHz, d_6-DMSO): δ = 2.30 (s, 3H, CH_3), 7.35 (m, 2H, 3bz*H*), 7.42 (dd, $^{3}J_{HH}$ = 8.1, 4.7 Hz, 1H, 3bz*H*), 7.50 (ddd, $^{3}J_{HH}$ = 7.1, $^{4}J_{HH}$ = 1.7, 1.5 Hz, 3bz*H*), 7.84 (dd, $^{4}J_{HH}$ = 1.8, 1.5 Hz, 1H, 3bz*H*), 8.12 (ddd, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 2.3, 1.7 Hz, 1H, 3py*H*), 8.50 (dd, $^{3}J_{HH}$ = 4.7 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, 3py*H*), 9.00 (d, $^{4}J_{HH}$ = 1.7 Hz, 1H, 3py*H*), 9.64 (s, 1H, N*H*), 12.78 (br. s, 1H, CO_2H). ^{13}C(100 MHz, d_6-DMSO): δ = 13.22, 114.19, 117.43, 120.52, 123.85, 129.65, 132.82, 131.99, 135.03, 139.70, 146.43, 147.08, 148.87, 168.10. ν_{max}/cm^{-1} 3288w, 2375w, 2343w, 2111, 1858w, 1672m, 1572s, 1474m, 1412m, 1305m, 1241s, 1169m, 1126m, 1042s, 964m, 894s, 799s, 763s. ESI-MS^{+} (m/*z*) 203.1 [M-Py+Na]$^{+}$ (calculated for $C_9H_9N_2O_2Na^{+}$, 200.2) 100%; 256.0 [M+H]$^{+}$ (calculated for $C_{14}H_{14}N_3O_2^{+}$, 256.3) 39%. ESI-MS^{-}(m/*z*) 254.1 [M-H]$^{-}$, (calculated for $C_{14}H_{12}N_3O_2^{-}$, 254.3) 100%; 135.0 [M-COOH-Bz]-, (calculated for $C_7H_8N_3^{-}$, 134.2) 38%.

3py4bzH: 4-hydrazinobenzoic acid (0.58 g, 3.83 mmol) was suspended in acetonitrile (50 mL). 3-acetylpyridine (0.45 mL, 4.07 mmol) was added to the suspension. The reaction mixture was heated under reflux conditions overnight. A yellow precipitate was formed which was recovered by vacuum filtration and dried in air. Yield 0.90 g (92%). m.p. 292-293 °C. Found C, 65.35; H, 5.09; N, 16.44%; $C_{14}H_{13}N_3O_2$ requires C, 65.29; H, 5.19; 16.31%. ^{1}H(400 MHz, d_6-DMSO): δ = 2.32 (s, 3H, CH_3), 7.31 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, 4bz*H*), 7.42 (dd, $^{3}J_{HH}$ = 8.1, 4.7 Hz, 1H, 3py*H*), 7.83 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, 4bz*H*), 8.16 (ddd, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 2.2, 1.6 Hz, 1H, 3py*H*), 8.52 (dd, $^{3}J_{HH}$ = 4.7 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1H, 3py*H*), 9.00 (d, $^{4}J_{HH}$ = 2.2 Hz, 1H, 3py*H*), 9.87 (s, 1H, N*H*), 12.21 (br. s, 1H, CO_2H). ^{13}C(100 MHz, d_6-DMSO): δ = 13.38, 112.62, 121.35, 123.86, 131.46, 133.08, 134.82, 141.28, 147.25, 149.16, 149.78, 167.81. ν_{max}/cm^{-1} 3293w, 3258w, 2344w, 2115w, 1909w, 1675w, 1603m, 1559m, 1526m, 1478m, 1411m, 1380w, 1317m, 1293m, 1259s, 1144s, 1119s, 1076s, 1042s, 1013m, 970m, 875m, 846m, 813m, 800m, 772s. ESI-MS^{+} (m/*z*) 256.0 [M+H]$^{+}$ (calculated for $C_{14}H_{14}N_3O_2^{+}$, 256.3) 100%.

4py3bzH: 3-hydrazinobenzoic acid (2.915 g, 19.16 mmol) was suspended in acetonitrile (250 mL). 4-acetylpyridine (2.25 mL, 20.35 mmol) was added into the suspension. The reaction mixture was placed under reflux conditions overnight. A yellow precipitate was recovered by vacuum filtration. Yield 3.71 g (76%). m.p. 300-301 °C. Found C, 65.69; H, 4.99; N, 16.46%; $C_{14}H_{13}N_3O_2$ requires C, 65.86; H, 5.14; 16.46%. ^{1}H(400 MHz, d_6-DMSO): δ = 2.27 (s, 3H, CH_3), 7.37 (dd, 1H, $^{3}J_{HH}$ = 7.8, 7.6 Hz, 1H, 3bz*H*), 7.41 (ddd, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.6, 1.5 Hz, 1H, 3bz*H*), 7.54 (ddd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.8, 1.5 Hz, 1H, 3bz*H*), 7.71 (d, $^{3}J_{HH}$ = 6.2 Hz, 2H, 4py*H*), 7.88 (dd, $^{4}J_{HH}$ = 1.8, 1.6 Hz, 1H, 3bz*H*), 8.56 (d, $^{3}J_{HH}$ = 6.2 Hz, 2H, 4py*H*), 9.77 (s, 1H, N*H*), 12.74 (br. s, 1H, CO_2H). ^{13}C(100 MHz, d_6-DMSO): δ = 12.71, 114.42, 117.62, 119.86, 120.99, 129.71, 132.10, 139.18, 146.07, 146.37, 150.24, 168.04. ν_{max}/cm^{-1} 3469w, 3314m, 3053w, 2913w 2760w, 2374w, 2082w, 1882w, 1670m, 1569s, 1486s, 1414m, 1282m, 1230s, 1208s, 1157s, 1057m, 1012s, 880m, 814s, 752s. ESI-MS^{+} (m/*z*) 203.1 [M-Py+Na]$^{+}$ (calculated for $C_9H_9N_2O_2Na^{+}$, 200.2) 100%; 256 [M+H]$^{+}$ (calculated for $C_{14}H_{14}N_3O_2^{+}$) 24%. ESI-MS^{-} (m/*z*) 254.1 [M-H]$^{-}$ (calculated for $C_{14}H_{12}N_3O_2^{-}$) 100%; 135.0 [M-COOH-Bz]- (calculated for $C_7H_8N_3^{-}$, 134.2) 32%.

4py4bzH: 4-hydrazinobenzoic acid (2.92 g, 19.16 mmol) was suspended in acetonitrile (250 mL). 4-acetylpyridine (2.25 mL, 20.35 mmol) was added to the suspension. The reaction mixture was heated under reflux conditions overnight. A yellow precipitate was formed which was recovered by vacuum filtration, washed with diethyl ether (50 mL) and dried in air. Yield 3.46 g (71%). m.p. 327-328 °C. Found C, 65.58; H, 5.10; N, 16.46%; $C_{14}H_{13}N_3O_2$ requires C, 65.86; H, 5.14; N, 16.46%. ^{1}H(400 MHz, d_6-DMSO): δ = 2.29 (s, 3H, CH_3), 7.34 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, 4bz*H*), 7.74 (d, $^{3}J_{HH}$ = 6.2 Hz, 2H, 4py*H*), 7.85 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, 4bz*H*), 8.57 (d, $^{3}J_{HH}$ = 6.2 Hz, 2H, 4py*H*), 10.02 (s, 1H, N*H*), 12.11 (br. s, 1H, CO_2H). ^{13}C(100 MHz, d_6-DMSO): δ = 12.88, 112.90, 120.07, 121.85, 131.46, 140.78, 146.16, 149.47, 150.27, 167.76. ν_{max}/cm^{-1} 3279m, 3088w, 3037w, 2789w, 2373w, 2113w, 2083w, 1885w, 1670m, 1572s, 1525m, 1493m, 1413m, 1319m, 1248s, 1208m, 1151s, 1013s, 956m, 851s, 800s, 773s. ESI-MS^{+}(m/*z*) 256.0 [M+H]$^{+}$ (calculated for $C_{14}H_{14}N_3O_2^{+}$, 256.3) 100%.

Synthesis of Coordination Compounds

Poly-{[Zn(3py4bz)$_2$]·2DMF} (**1Zn**·2DMF): Zn(NO$_3$)$_2$·6H$_2$O (12 mg, 0.039 mmol) and 3py4bzH (20 mg, 0.078 mmol) were added to DMF (3 mL) and sonicated to dissolve. The solution was heated at 100 °C overnight to form colourless crystals. Yield 3.2 mg (15%). Found, C, 55.17; H, 5.35; N, 14.57%. $C_{34}H_{40.5}N_{7.5}O_{5.5}Zn$ (**1Zn**·1.5DMF·1.5H$_2$O) requires C, 54.93; H, 5.32; N, 14.78% (apparent moisture uptake in transit). ν_{max}/cm^{-1} 3249w, 2863w, 2509w, 2322w, 2104w, 1919w, 1802w, 1670m, 1600s, 1566m, 1545m, 1522m, 1497m, 1396s, 1324m, 1195m, 1157m, 1137m, 1092m, 1052m, 1024m, 972m, 853m, 784s, 695s, 651m.

Poly-{[Cd(3py4bz)$_2$]·2DMF} (**1Cd**·2DMF): Cd(NO$_3$)$_2$·4H$_2$O (12 mg, 0.039 mmol) and 3py4bzH (20 mg, 0.078 mmol) were added to DMF (3 mL) and sonicated to dissolve. The solution was heated at 100 °C overnight to form orange crystals. Yield 1.4 mg (6%). Found, C, 53.18; H, 5.13; N, 14.55%. $C_{34}H_{38}N_8O_6Cd$ requires C, 53.23; H, 4.99; N, 14.65%. ν_{max}/cm^{-1} 3237w, 3057w, 2917w, 2839w, 2344w, 2117w, 2085w, 1918w, 1677m, 1602m, 1570m, 1523m, 1490m, 1379s, 1322m, 1252s, 1193m, 1154m, 1136m, 1088m, 1047m, 955m, 850s, 805m, 782s.

Poly-{[Cu(3py4bz)$_2$]·DMF} (**1Cu**·DMF): Cu(NO$_3$)$_2$·3H$_2$O (9 mg, 0.039 mmol) and 3py4bzH (20 mg, 0.078 mmol) were added to DMF (3 mL) and sonicated to dissolve. The solution was heated at 100 °C overnight to form orange crystals. Yield 8 mg (29%). ν_{max}/cm^{-1} 1656w, 1598m, 1546m, 1510w, 1364s, 1302w, 1251s, 1152w, 1133w, 1092m, 1055w, 835w, 783s, 693s. Microanalysis was precluded by the presence of a small amount of an intractable brown amorphous co-product; however, PXRD confirms the identity of the bulk product (see ESI).

Poly-{[Zn(3py4bz)$_2$]·H$_2$O} (**1Zn**·H$_2$O): Zn(NO$_3$)$_2$·6H$_2$O (12 mg, 0.039 mmol) and 3py4bzH (20 mg, 0.078 mmol) were added to a 1:1 mixture of DMF and water (3 mL) and sonicated to dissolve. The solution was heated at 100 °C overnight to form colourless crystals. Yield 21 mg (89%). Found, C, 55.08; H, 4.86; N, 13.85%. $C_{28}H_{28}N_6O_6Zn$ (**1Zn**·2H$_2$O) requires 55.14, 4.63, 13.78. ν_{max}/cm^{-1} 3400m, 3266m, 1655w, 1598s, 1545m, 1522m, 1372s, 1253s, 1155s, 1102m, 1051m, 851m, 783s, 693s.

Poly-{[Co(4py3bz)$_2$]·3.5DMF} (**2**·3.5DMF): Co(NO$_3$)$_2$·6H$_2$O (12 mg, 0.039 mmol) and 4py3bzH (20 mg, 0.078 mmol) were added to DMF (3 mL) and sonicated to dissolve. The solution was heated at 100 °C for 3 days to form orange/red crystals. Yield 29 mg (95%). Found, C, 53.92; H, 4.65; N, 13.74%. $C_{28}H_{30}N_6O_7Co$ (**2**·3H$_2$O) requires C, 54.11; H, 4.87; N, 13.52%. (Note, compound rapidly loses crystallinity upon standing in air, believed to be solvent exchange, and PXRD suggests impurity present in the bulk). ν_{max}/cm^{-1} 1658s, 1606w, 1564m, 1494w, 1383s, 1248m, 1216m, 1156w, 1092m, 1061w, 1016m, 832m, 764m, 689m, 659m.

Poly-{[Zn(3py3bz)$_2$]·2.5H$_2$O} (**3Zn**·2.5H$_2$O): Zn(NO$_3$)$_2$·6H$_2$O (7 mg, 0.0195 mmol) was dissolved in methanol (1 mL) and added to a solution of 3py3bzH (10 mg, 0.039 mmol) in methanol (2 mL). The solution was left overnight at room temperature to form orange crystals. Yield 1.3 mg (9%). Found, C, 54.41; H, 4.86; N, 13.56%. $C_{28}H_{29}N_6O_{6.5}Zn$ ([Zn(3py3bz)$_2$]·2.5H$_2$O) requires C, 54.50; H, 4.74; N, 13.62%. ν_{max}/cm^{-1} 3243w, 2322w, 2222w, 2121w, 2089w, 1905w, 1701w, 1593m, 1541s, 1486m, 1448m, 1398s, 1330m, 1308m, 1249s, 1147m, 1123m, 1086m, 1051s, 1019m, 996m, 931m, 891m, 846m, 814m, 788m, 762s.

Poly-{[Cd(3py3bz)$_2$]·0.4H$_2$O} (**3Cd**·0.4H$_2$O): Cd(NO$_3$)$_2$·4H$_2$O (7 mg, 0.0195 mmol) was dissolved in methanol (1 mL) and added to a solution of 3py3bzH (10 mg, 0.039 mmol) in methanol (2 mL). The solution was left overnight at room temperature to form orange crystals. Yield 1.2 mg (9%). Found, C, 53.83; H, 4.26; N, 13.37%. $C_{28}H_{24.8}CdN_6O_{4.4}$ ([Cd(3py3bz)$_2$]·0.4H$_2$O) requires C, 53.54; H, 3.98; N, 13.38%. ν_{max}/cm^{-1} 3265w, 2125w, 1930w, 1593w, 1535s, 1487m, 1439m, 1391s, 1330m, 1309m, 1249s, 1148m, 1123m, 1084m, 1048m, 1022m, 996m, 893m, 843m, 812m, 786m, 763s.

Poly-{[Ni(4py4bz)$_2$]·2H$_2$O} (**4Ni**·2H$_2$O): 4py4bzH (20 mg, 0.078 mmol) and Ni(NO$_3$)$_2$·6H$_2$O (11 mg, 0.039 mmol) were added to DMF (3mL) and sonicated to dissolve. The solution was heated at 100°C overnight to form green crystals. Yield 3.8 mg (19%). Found C, 55.51; H, 4.53; N, 13.80 %; $C_{28}H_{24}N_6NiO_4$·2H$_2$O requires C, 55.75; H, 4.69, N, 13.93%. (Note, the SQUEEZE routine applied to diffraction data suggests a higher degree of solvation). ν_{max}/cm^{-1} 1657s, 1602m, 1563w, 1493w, 1383s, 1252m, 1217w, 1156w, 1091s, 1061m, 1014w, 831w, 781w, 687w, 659m.

Poly-{[Co(4py4bz)$_2$]·2H$_2$O} (**4Co**·2H$_2$O): 4py4bzH (20 mg, 0.078 mmol) and Co(NO$_3$)$_2$·6H$_2$O (11 mg, 0.039 mmol) were added to DMF (3mL) and sonicated to dissolve. The solution was heated at 100°C overnight to form red crystals. Yield 12.0 mg (54%). Found, C, 55.81; H, 4.70; N, 13.55%. $C_{28}H_{24}N_6CoO_4$·2H$_2$O requires C, 55.73; H, 4.68; N, 13.93%. (Note, the SQUEEZE routine applied to diffraction data suggests a higher degree of solvation). ν_{max}/cm^{-1} 1665m, 1602m, 1570m, 1525m, 1488m, 1400s, 1323w, 1251s, 1217m, 1157m, 1139m, 1088m, 1019m, 852m, 830w, 782s, 688m, 659w.

Crystallography

Data was collected using either a Bruker ApexII diffractometer or the MX1/MX2 beamlines at the Australian Synchrotron.[11] The ApexII diffractometer was equipped with Mo-Kα radiation (λ = 0.71073 Å) and samples were maintained at 123 K during the collection. Data collection, indexing and integration were conducted using the SAINT software package.[12a] Absorption corrections were applied using SADABS.[12b]

The synchrotron beamlines were operating at 17.4 keV (λ = 0.7108 Å) and sample temperatures were maintained at 100 K during the collection. Data collection was controlled using the

BluICE GUI.[13a] Data processing was conducted using the XDS program suite.[13b]

Structures were solved using either SHELXT or by direct methods using SHELXS-2014.[14] Structures were refined by standard least squares methods against F^2 using SHELXL-2014. The programs X-Seed and Olex2 were used as graphical interfaces.[15] All non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms attached to carbon were placed in idealised X-ray positions and refined using a riding model. Hydrogen atoms attached to oyxgen or nitrogen were located from the Fourier difference map and refined with restrained X-H distances and U_{iso} values of 1.2 or 1.5 times that of the isotropic equivalent of the carrier atom. Crystallographic refinement parameters for all structures are given in Tables 1 and 2. Additional non-standard refinement details for individual structures is given in the Supporting Information, including the use of the SQUEEZE routine of PLATON for the structures of **3** and **4**.[16]

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and are available from www.ccdc.cam.ac.uk (CCDC deposition numbers 1477012-1477024).

Results and Discussion

Ligand Structures

Four isomeric ligands were synthesised from the corresponding hydrazinobenzoic acid and acetylpyridine isomers in good yields (Figure 2). The molecules are rigid and planar and therefore have the two differently functionalised terminal groups locked in a set conformation, with the only rotational freedom being the orientation of the meta-substituted rings. All four of the ligands were able to be crystallised and structurally characterised, showing similar structural motifs, in terms of intermolecular interactions, but quite different packing arrangements due to the geometrical differences.

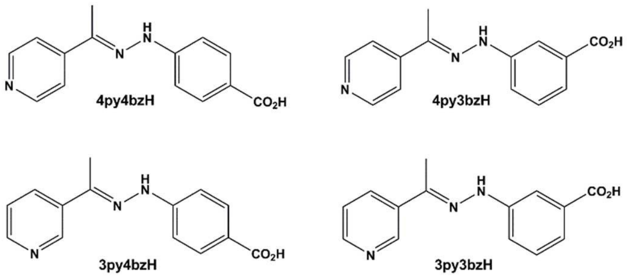

Figure 2: The four isomeric, heterotopic ligands used in this study (naming derived from substitution positions of functional groups).

The structure of **3py4bzH** unexpectedly forms in the non-centrosymmetric space group *P*1 with Z′ = 6.[17] Evaluation of this structural model, both by eye and using the ADDSYM tool of PLATON, shows only pseudo-inversion symmetry that applies to four of the molecules in the *P*1 cell with the remaining two molecules having no symmetry relationship.[16a] The structure is best viewed as 1D chains of the molecule, which is near perfectly planar, that are held together by hydrogen bonds between the carboxylic acid and the pyridyl nitrogen atom with an average O···N distance of 2.59 Å (Figure 3, a table of hydrogen bonding parameters is given in ESI).

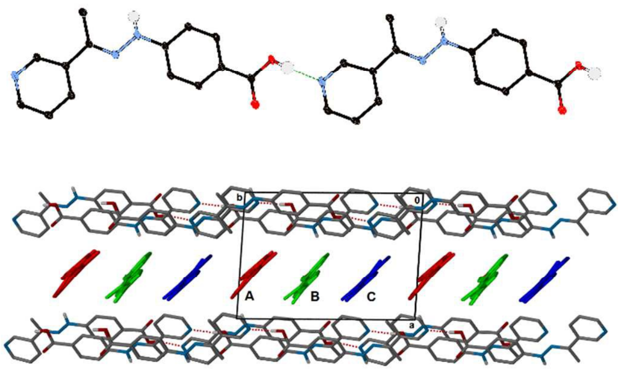

Figure 3: (top) The carboxylic acid-pyridyl interaction that forms 1D chains in the structure of 3py4bzH. (bottom) Packing of the structure viewed down the *c*-axis highlighting the repeating pattern of the hydrogen-bonded chains; chains A and C are related by a pseudo-inversion centre whilst chain B breaks this symmetry to yield the acentric *P*1 structure (inter-layer NH···O hydrogen bonds not shown for clarity).

Each of the crystallographically unique molecules in the structure of **3py4bzH** forms a 1D chain in this manner through interactions solely with its own equivalents generated by translation, giving six unique chains. Three of the chains lie parallel to the *b*-axis and three lie parallel to the *c*-axis forming pi-stacked layers in which the chains are orthogonally aligned. Between these layers are NH···O hydrogen bonds involving the hydrazone NH groups and the C=O group of the carboxylic acids (average N···O distance 2.97 Å) in five of the six unique molecules. For the sixth unique NH···O interaction the accepting group is the COH of the carboxylic acid. It is quite remarkable that one out of the six interactions is unique in this respect. In each sheet the three crystallographically unique chains are stacked in an A-B-C-A-B-C manner (Figure 3). The A and C chains are aligned in an anti-parallel fashion and are related by a pseudo-inversion centre. The B chain is aligned in the same direction as C, however there is no inversion equivalent and hence the structure remains *P*1. The structure of **4py4bzH** was solved in the space group *Pna*2_1 and contains a single molecule in the asymmetric unit. As with **3py4bzH**, the molecule is near perfectly planar and the CO_2H···py hydrogen bond synthon holds together 1D chains of the molecule. Adjacent chains interact by means of hydrogen bonds between the hydrazone NH and the C=O of the carboxylic acids (Figure 4). These hydrogen bonds form a 3D network; three such networks are interpenetrated in the overall structure with face-to-face π interactions between them (see supporting information).

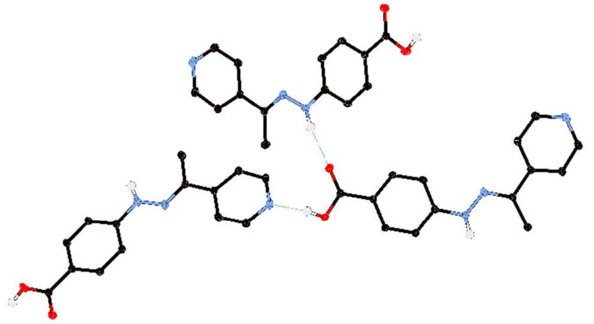

Figure 4: Hydrogen bonding interactions in the structure of **4py4bzH**. CH hydrogen atoms are omitted for clarity.

The **3py3bzH** molecule is somewhat different to the other three ligands as it does not possess a para-positioned functional group and therefore is not arranged in a geometry suited to forming hydrogen-bonded chains. The structure of **3py3bzH** was solved in $P2_1/n$ and contains a single molecule in the asymmetric unit. The hydrogen bonding interactions are similar to the previous two structures, i.e. the carboxylic acid acts as a hydrogen-bond donor to the pyridyl nitrogen and accepts a hydrogen bond from the hydrazone NH. The substitution pattern of the ligand allows for a cyclic motif to be formed between two ligands involving the OH···N interactions (Figure 5). These rings are connected through NH···O interactions to form corrugated 2D sheets that then stack through face-to-face π-interactions. A similar ring motif is observed in the coordination polymers containing the **3py4bz** and **4py3bz** ligands (**1** and **2**, respectively), with the difference in subsitution pattern reflecting the coordination requirements of the metal ions vs. the geometry required for simple hydrogen bonding in the case of the struture of **3py3bzH**.

Crystals of **4py3bzH** could only be obtained as a DMF solvate and were solved in the space group $P2_1/n$. The molecules are arranged in a 1D chain mediated again by hydrogen-bonding interactions between the carboxylic acid and the pyridyl nitrogen atom. The presence of DMF prevents the formation of NH···O interactions between the hydrazone and the carboxylic acid and instead there is an interaction between the hydrazone and the solvent.

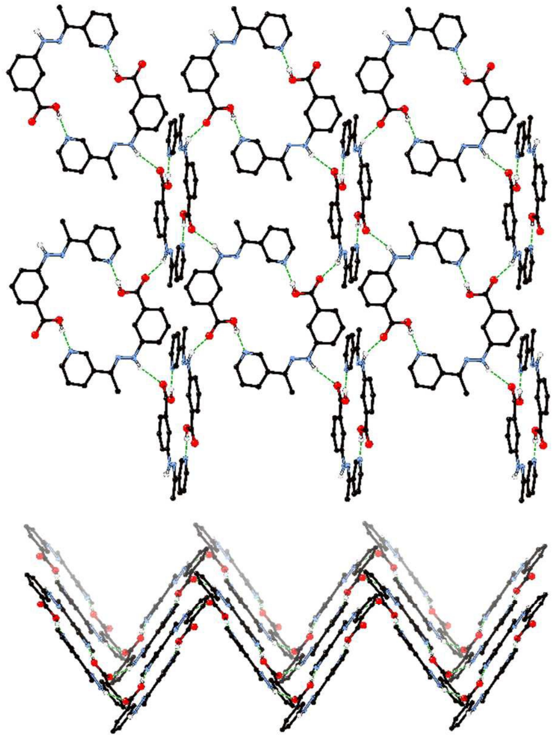

Figure 5: Offset views of a 2D hydrogen-bonded sheet in the structure of **3py3bzH** perpendicular to the sheet (top) and coincidental with the sheet (bottom).

Coordination Polymers of 3py4bz and 4py3bz

The two mixed meta/para substituted ligands, **3py4bzH** and **4py3bzH**, both form centrosymmetric coordination polymers. Reaction of **3py4bzH** with a variety of transition metal salts yields 1D coordination polymers of the form $[M(3py4bz)_2]$, with differences in the geometry of the chain brought about by the use of different metal ions, whilst **4py3bzH** forms a 2D network containing a similar structural motif.

Cadmium and zinc form isostructural materials $[M(3py4bz)_2]\cdot 2DMF$ (**1M**·2DMF) with one formula unit contained in the asymmetric unit of the *P*-1 cell. The 1D coordination polymers consist of loops that lie almost perpendicular to the neighbouring loops of the chain. The metal ions are, as expected, six coordinate and bound by two carboxylate groups and two pyridyl groups from four separate ligands. This coordination mode is expected from mixed pyridyl/carboxylate ligands and there are no solvent molecules in the coordination sphere. The ligands are almost perfectly planar. The metal centres adopt a distorted octahedral geometry due to the chelating carboxylates with these bidentate groups having asymmetric coordination in all but one instance (see Figure 6). Whilst the anticipated coordination mode is observed, the 1D polymers contain inversion centres at the midpoints of the loops in the centrosymmetric structure. One of the hydrazone NH groups forms a hydrogen bond to a carboxylate of a neighbouring chain whilst the other crystallographically unique NH forms a hydrogen bond to one of the lattice DMF molecules. The remaining DMF does not take part in any significant supramolecular interactions and is consequently disordered over two positions at one site in the lattice. In addition to the NH···O hydrogen bonding, neighbouring chains pack with face-to-face π interactions between benzoate and pyridyl rings.

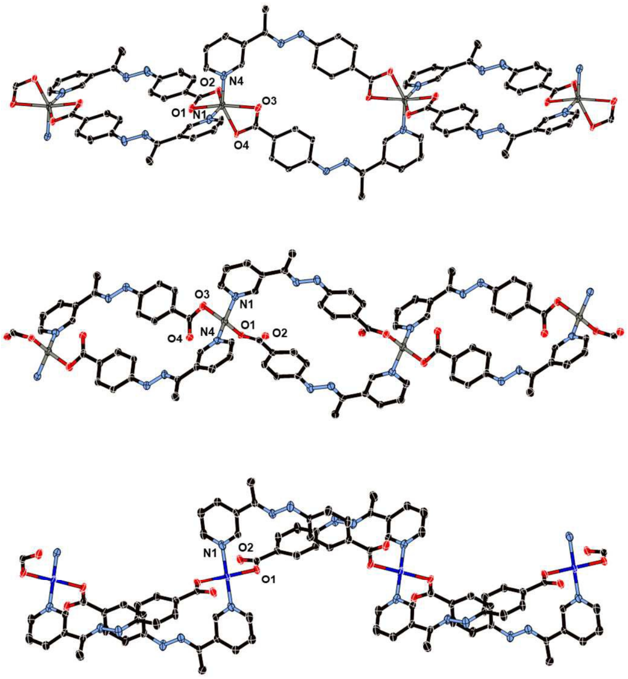

Figure 6: (Top) Part of the 1D chain in the structure of $[Zn(3py4bz)_2]\cdot 2DMF$ (**1Zn**·2DMF) which is isostructural with the cadmium analogue (**1Cd**·2DMF). (Middle) Part of the 1D chain in the structure of $[Zn(3py4bz)_2]\cdot H_2O$ in which the Zn^{II} ions are tetrahedral (**1Zn**·H_2O). (Bottom) Part of the 1D chain in **1Cu**·DMF in which the rings are non-planar due to the square planar metal coordination geometry. Hydrogen atoms are omitted for clarity. Selected distances (Å): **1Cd**·2DMF; Cd-O1, 2.3970(17); Cd-O2, 2.2971(18); Cd-O3, 2.4130(17); Cd-O4, 2.2625(17). **1Zn**·2DMF; Zn-O1, 2.1740(14); Zn-O2, 2.1860(14); Zn-O3, 2.2373(14); Zn-O4, 2.1088(14). **1Zn**·H_2O; Zn-O1, 1.944(3); Zn-O2, 2.815; Zn-O3, 1.980(3); Zn-O4, 2.774. **1Cu**·DMF; Cu-O1, 1.934(3); Cu-O2, 2.679.

The zinc-containing compound was also obtained as a hydrate, $[Zn(3py4bz)_2]\cdot H_2O$, rather than a DMF solvate (**1Zn**·H_2O) from a reaction using 1:1 DMF:H_2O rather than neat DMF. The coordination polymer itself is again a 1D chain consisting of loops, but the spatial arrangement of the ligands is somewhat different and the zinc adopts a tetrahedral rather than octahedral coordination geometry (Figure 6). The carboxylate groups in **1Zn**·$2H_2O$ coordinate in a monodentate fashion with the longest Zn-O distances being clearly outside of any possible interaction (*ca.* 2.8 Å). The ligands are not planar, with the benzoate groups of the ligands rotated by an average of 14 ° with respect to the pyridyl-hydrazone part of the molecule and the CO_2 group itself twisted by an average of 30 ° with respect to the aromatic ring. Overall this make the loops in the chain narrower in **1Zn**·H_2O than in **1Zn**·2DMF. It is reasonable to attribute these differences to the presence of water, rather than DMF, and its role as both hydrogen bond donor and acceptor. The water in **1Zn**·H_2O acts as a hydrogen bond acceptor to one of the hydrazone NH groups, similar to DMF in **1Zn**·2DMF. However, the water acts as a hydrogen bond donor to two carboxylate oxygen atoms, one coordinated and one non-coordinated. The remaining non-coordinated carboxylate oxygen atom accepts a hydrogen bond from the second hydrazone NH group.

The structure of $[Cu(3py4bz)_2]\cdot DMF$ (**1Cu**·DMF) is considerably different to that in the zinc and cadmium analogues despite retaining a 1D chain comprising loops. The change in metal ion alters the coordination geometry at the node with the copper(II) adopting a square planar geometry and lying on a crystallographic inversion centre, which is not unusual for this combination of metal/ligands.[18] The two pyridyl and two monodentate carboxylate ligands are in a mutually *trans* arrangement, in contrast to the *cis* arrangement in **1Zn**/**1Cd**·2DMF and the tetrahedral arrangement in **1Zn**·H_2O. Whilst in the previous 1D chains the ligands within each loop are close to being co-planar, those in **1Cu**·DMF are in a 'pinched' conformation with adjacent loops being on alternate faces of the chain. There is a minor deviation from planarity in the ligands, presumably to allow these chains to form, with the pyridyl ring rotated by *ca.* 21 ° with respect to the plane of the rest of the molecule. The structure contains only one crystallographically unique ligand (i.e. half of the formula unit is contained in the asymmetric unit). The NH of the hydrazone group forms a hydrogen bond to the non-coordinating oxygen atom of a carboxylate, serving to connect all adjacent chains by hydrogen bonding into a 3D network. The DMF molecules reside disordered in the lattice with no significant supramolecular interactions (50:50 occupancy across two overlapping symmetry-related orientations).

Overall, the various structures of **1** show a remarkable persistence of the 1D chain motif despite considerable changes in the metal coordination environment. To some extent this is presumably driven by the combination of carboxylate and pyridyl donor groups that exclude coordinating solvent from the structures and the geometry of the ligand is such that the 1D motif is the best way to accommodate the coordination of both ends of the ligand.

Reaction of **4py3bzH** with $Co(NO_3)_2$ yielded the 2D coordination polymer $[Co(4py3bz)_2]\cdot 3.5DMF$ (**2**·3.5DMF) which contains some structural similarities to **1Zn**, presumably due to the analogous substitution pattern in the ligand (*i.e.* one meta and one para functional group). The Co^{II} atoms are each coordinated by two pyridyl groups and two carboxylate groups in a pseudo-tetrahedral arrangement. Notably there exists a ring motif bewteen pairs of metals, with the rings then bridged by a non-equivalent ligand to form a 2D sheet (Figure 7).

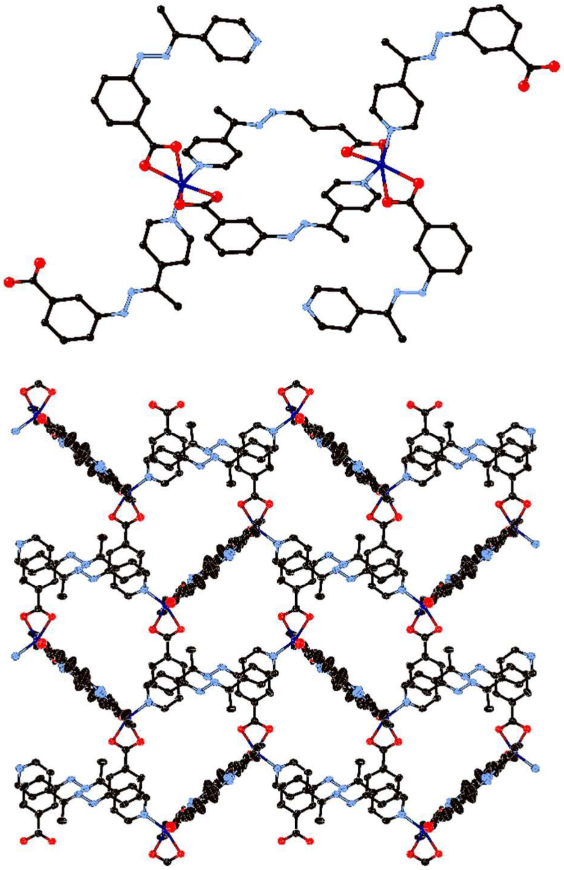

Figure 7: (Top) One of the ring motifs in the structure of **2**, analogous to those in **1Zn** and **1Cd**, *c.f.* Figure 6. (Bottom) 'Top-down' view of a 2D sheet in the structure of **2** showing the connections between the ring motifs which are oriented into the page.

The geometric similarity between the **4py3bz** and **3py4bz** ligands allows a very similar ring motif to form in both **1** and **2**, with the closest comparison being with the **1Zn** chain. The centrosymmetric ring in **2** is close to planar, although this is somewhat hard to determine categorically as the ligands are disordered across two positions. The slight differences between the ligands in **1Zn** and **2** have an effect on the distance between the metal ions in the ring, with metal···metal distances of 11.5 Å and 10.3 Å, respectively. In the structure of **2**, each ring is connected to four others to form the 2D sheet. The ring motifs are orientated perpendicular to the plane of the sheet and the ligands that connect the rings together are involved in π–stacking interactions (Figure 7). The lattice DMF molecules reside in the windows of the sheet, with one unit occupancy molecule participating in a hydrogen-bonding interaction with the hydrazone group of the non-disordered ligand and the other two, which are modelled at partial occupancy, only participating in weak CH···O interactions. Small voids in the structure appear to contain unresolved DMF (see ESI).

Coordination Polymers of 3py3bz and 4py4bz

The ligands **3py3bzH** and **4py4bzH** both yield acentric, isomorphous series, with the composition [M(3py3bz)$_2$]·solvent (M = Zn, **3Zn**; M = Cd, **3Cd**) and [M(4py4bz)$_2$] ·solvent (M = Ni, **4Ni**; M = Cu, **4Cu**), when reacted with a variety of transition metal salts (see experimental section for discussion of lattice solvents). In both instances the structures contain non-centrosymmetric 4,4 sheets that pack in a helical manner (Figure 8). The structures of both **3** and **4** contain octahedral metal centres coordinated by two pyridyl groups and two carboxylate groups, the same coordination environment that exists in all of the structures mentioned herein.

The structures of compounds **3** and **4** were solved in the space groups P4$_1$2$_1$2 and P3$_1$21, or their opposite form, respectively, with the metal centres coincident with 2-fold axes in both cases. It should be emphasised that for both series of compounds, crystals were obtained in the two possible space group isomers, i.e. despite what is commonly refered to as 'spontaneous resolution' (chiral crystals from achiral components) there is no bulk chirality associated with the product which forms as a racemic mixture. The non-centrosymmetric sheets in both **3** and **4** pack due to the arrangement of the heterotopic ligands as intended (*c.f.* Figure 1). In both cases the sheets pack in a helical manner (it is also feasible that an overall centrosymmetric structure could have resulted with 'head-to-tail' packing of the sheets).

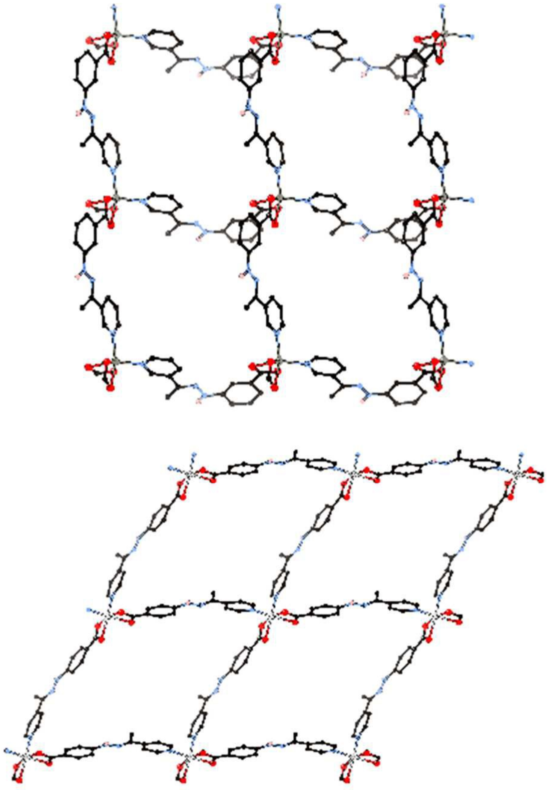

Figure 8: Side-by-side comparison of the non-centrosymmetric 4,4 sheets of [Zn(3py3bz)$_2$] (**3Zn**, top) and [Ni(4py4bz)$_2$] (**4Ni**, bottom) with CH hydrogen atoms omitted for clarity.

The 2D sheets in the structure of **3** pack closely due to face-to-face π-interactions, with each ligand involved in interactions with two others, supported by NH···O hydrogen bonds between the hydrazone and a coordinated carboxylate (Figure 9). The sheets themselves are regular square grids that lie perpendicular to the four-fold screw axis. The π-interactions exist between the pyridyl ring of one ligand and the benzoate ring of a neighbouring ligand although these interactions are not reciprocated within a pair of ligands but involve three ligands overall (*i.e.* one ligand forms interactions with two others in this manner). These interactions propogate parallel to the non-unique tetragonal axes (as can be seen both face-on and side-on in Figure 9). The NH···O hydrogen bonds occur between a perpendicular pair of ligands that are not involved in π-interactions. The sheets are offset such that the metal ions of one sheet lie directly centred above/below the holes in adjacent sheets and therefore no voids/channels exist in the overall structure.

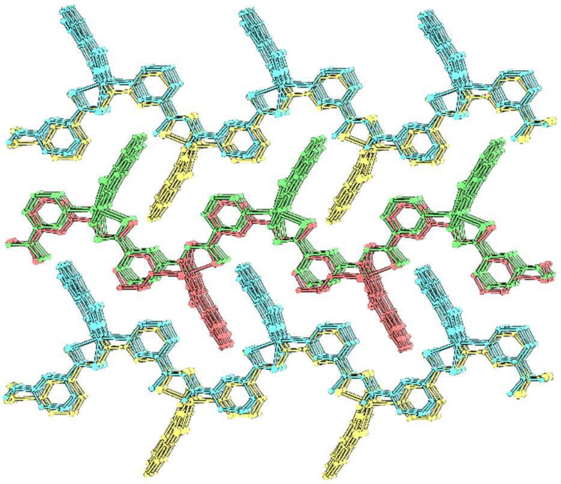

Figure 9: Packing of the 2D sheets in the structure of **3**, viewed along a non-unique tetragonal axis. CH hydrogen atoms are omitted for clarity.

Similar to the structure of **3**, the 2D sheets in the structure of **4** pack by virtue of face-to-face π-interactions. Rather than a regular square grid, the (4,4) sheets contain parallelogram windows with internal angles between the metal-metal vectors of 60° and 120°. The intermolecular interactions are remarkably similar to those in the structure of **3**. Again, each ligand interacts with two others from one adjacent sheet through face-to-face π-interactions between pyridyl and benzoate rings in addition to NH···O hydrogen bonds between sheets (Figure 10). The sheets are not packing in an overlapping manner leaving small hexagonal channels, that run parallel to the unique axis, into which the methyl groups are directed. There are also channels that run perpendicular to this direction with both containing solvent that could not be identified crystallographically. Any attempts to remove the solvent resulted in complete loss of crystallinity, presumably due to the relatively weak interactions holding the layers together.

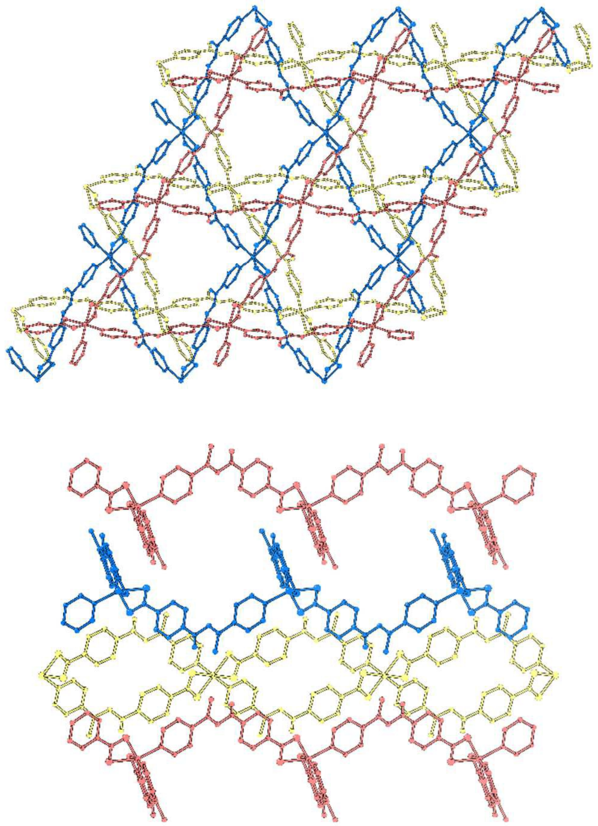

Figure 10: The packing of **4** viewed along the unique hexagonal axis (top) and along a non-unique axis (bottom). CH hydrogen atoms omitted for clarity.

Conclusions

The four isomeric, heterotopic ligands ligands demonstrate both the applicability and potential issues with using low-symmetry achiral ligands to synthesise chiral materials. The mixed pyridyl/carboxylate ligands have the notable advantage of completely filling the metal coordination sphere and removing any structural uncertainty associated with coordianted solvent whilst giving an acentric coordination environment in all materials with the exception of **1Cu**. The ligands with mixed meta/para substitution patterns (**3py4bz** and **4py3bz**) formed centrosymmetric coordination polymers, both featuring a similar ring motif. These materials demonstrate a robustness of the ring motif but also demonstrate the unreliablilty associated with such attempts to form acentric materials. The **3py3bz** and **4py4bz** ligands form non-centrosymmetric (4,4) sheets with different geometries which influences the manner in which they pack. These ligands cannot form closed 2-membered rings. In both **3** and **4** the sheets pack in a helical manner, facilitated by both face-to-face π-interactions and NH···O hydrogen bonds, with helical channels generated in the latter case (albeit unstable to desolvation). These results demonstrate that the use of low-symmetry heterotopic ligands is a viable route to racemic chiral materials, although there remains some unpredictability in the self-assembly process and the importance of ligand geometry appears paramount.

Acknowledgements

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References

1 (a) B.F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546-1554. (b) S.R. Batten, S.M. Neville and D.R. Turner, *Coordination Polymers: Design, Analysis and Application*, 2009, Royal Society of Chemistry, Cambridge, UK.
2 (a) O.K. Farha and J.T. Hupp, *Acc. Chem. Res.*, 2010, **43**, 1166-1175. (b) N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933-969. (c) R. Robson, *Dalton Trans.*, 2008, 5113-5131. (d) B. Seoane, S. Castellanos, A. Dikhtiarenko, F. Kapteijn and J. Gascon, *Coord. Chem. Rev.*, 2016, **307**, 147-187.
3 (a) C. Janiak, *Dalton Trans.*, 2003, 2781-2804. (b) H. Furukawa, K.E. Cordova, M. O'Keeffe and O.M. Yaghi, *Science*, 2013, **341**, 1230444. (c) S.T. Meek, J.A. Greathouse and M.D. Allendorf, *Adv. Mater.*, 2011, **23**, 249-267. (d) S.L. Qiu and G.S. Zhu, *Coord. Chem. Rev.*, 2009, **253**, 2891-2911.
4 (a) D.R. Turner, in *Chirality in Supramolecular Assemblies*, ed. F.R. Keene, in press, 2016, Wiley Publishing, Oxford, UK. (b) W. Lin, *J. Solid State Chem.*, 2005, **178**, 2486-2490. (c) R.E. Morris and X. Bu, *Nature Chem.*, 2010, **2**, 353-361.
5 (a) E.Q. Gao, Y.F. Yue, S.Q. Bai, Z. He and C.H. Yan, *J. Am. Chem. Soc.*, 2004, **126**, 1419-1429. (b) L. Perez-Garcia and D.B. Amabilino, *Chem. Soc. Rev.*, 2007, **36**, 941-967.
6 (a) Z. Lin, A.M.Z. Slawin and R.E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 4880-4881. (b) Y. Kang, S. Chen, F. Wang, J. Zhang and X. Bu, *Chem. Commun.*, 2011, **47**, 4950-4952.
7 T. Ezuhara, K. Endo and Y. Aoyama, *J. Am. Chem. Soc.*, 1999, **121**, 3279-3283.
8 S.T. Wu, Z.W. Cai, Q.Y. Ye, C.H. Weng, X.H. Huang, X.L. Hu, C.C. Huang and N.F. Zhuang, *Angew. Chem. Int. Ed.*, 2014, **53**, 12860-12864.
9 (a) O.R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511-522. (b) O.R. Evans and W. Lin, *Chem. Mater.*, 2001, **13**, 3009-3017.
10 (a) P. Teo and T.S.A. Hor, *Coord. Chem. Rev.*, 2011, **255**, 273-289. (b) G. Mehlana, S.A. Bourne and G. Ramon, *Dalton Trans.*, 2012, **41**, 4224. (c) J. Sun, L. Weng, Y. Zhou, J. Chen, Z. Chen, Z. Liu and D. Zhao, *Angew. Chem. Int. Ed.*, 2002, **41**, 4471-4473. (d) G. Mehlana, S.A. Bourne, G. Ramon and L. Öhrström, *Cryst. Growth Des.*, 2013, **13**, 633-644. (e) S.K. Elasidi, M.H. Mohamed, L. Wojtas, A. Chanthapally, T. Pham, B. Space, J.J. Vittal and M.J. Zaworotko, *J. Am. Chem. Soc.*, 2014, **136**, 5072-5077.
11 N.P. Cowieson, D. Aragao, M. Clift, D.J. Ericsson, C. Gee, S.J. Harrop, N. Mudie, S. Panjikar, J.R. Price, A. Riboldi-Tunnicliffe, R. Williamson and T. Caradoc-Davies, *J. Synchrotron Rad.*, 2015, **22**, 187.
12 (a) *SAINT*, 2012, Bruker AXS Inc., Madison, Wisconsin, USA. (b) *SADABS*, 2001, Bruker AXS Inc., Madison, Wisconsin, USA.
13 (a) T.M. McPhillips, S.E. McPhillips, J.H. Chiu, A.E. Cohen, A.M. Deacon, P.J. Ellis, E. Garman, A. Gonzalez, N.K. Sauter, R.P. Phizackerley, S.M. Soltis and P.J. Kuhn, *J. Synchrotron Rad.*, 2002, **9**, 401-406. (b) W. Kabsch, *J. Appl. Crystallogr.*, 1993, **26**, 795-800.
14 G.M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3-8.
15 (a) O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339. (b) L.J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189-191.
16 (a) A.L. Spek, *Acta Crystallogr.*, 2009, **D65**, 148. (b) A.L. Spek, *Acta Crystallogr.*, 2015, **C71**, 9-18.
17 (a) J. W. Steed, *CrystEngComm*, 2003, **5**, 169. (b) G.R. Desiraju, *CrystEngComm*, 2007, **9**, 91. (c) K. M. Anderson, M. R. Probert, A. E. Goeta & J. W. Steed, *CrystEngComm*, 2011, **13**, 83. (d) R. E. Marsh, *Acta Crystallogr.*, 1999, **B55**, 931.
18 For example, (a) D. Ghosh, I. Lebedytė, D.S. Yufit, K.K. Damodaran and J.W. Steed, *CrystEngComm*, 2015, **17**, 8130-8138. (b) R.P. Sharma, A. Saini, D. Monga, P. Venugopalan, J. Jezierska, A. Ozarowski and V. Ferretti, *New J. Chem.*, 2014, **38**, 437-447.

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Table 1: Crystallographic and refinement parameters for structures of neutral ligands and coordination polymers containing **3py4bz**.

	3py3bzH	**3py4bzH**	**4py3bzH·DMF**	**4py4bzH**	**[Cd(3py4bz)$_2$]·2DMF (1Cd·2DMF)**	**[Zn(3py4bz)$_2$]·2DMF (1Zn·2DMF)**	**[Cu(3py4bz)$_2$]·DMF (1Cu·DMF)**	**[Zn(3py4bz)$_2$]·H$_2$O (1Zn·H$_2$O)**
Formula	$C_{14}H_{13}N_3O_2$	$C_{14}H_{13}N_3O_2$	$C_{17}H_{20}N_4O_3$	$C_{14}H_{13}N_3O_2$	$C_{34}H_{38}CdN_8O_6$	$C_{34}H_{38}N_8O_6Zn$	$C_{31}H_{31}CuN_7O_5$	$C_{28}H_{26}N_6O_5Zn$
M	255.27	255.27	328.37	255.27	767.12	720.09	645.17	591.92
Cell Setting	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic	Triclinic
Space Group	$P2_1/n$	$P1$	$P2_1/n$	$Pna2_1$	P-1	P-1	$C2/c$	P-1
a / Å	9.4840(19)	9.801(2)	9.875(2)	13.152(3)	10.156(2)	10.0203(4)	16.7033(17)	7.9650(16)
b / Å	14.148(3)	13.736(3)	9.4220(19)	8.4410(17)	11.554(2)	11.3836(4)	9.3648(9)	8.0400(16)
c / Å	9.994(2)	14.268(3)	18.577(4)	11.502(2)	15.972(3)	15.9371(5)	19.686(3)	20.311(4)
α / º	90	79.99(3)	90	90	83.61(3)	82.8520(10)	90	81.56(3)
β / º	109.45(3)	80.75(3)	104.92(3)	90	88.74(3)	87.3960(10)	108.139(5)	85.94(3)
γ / º	90	85.00(3)	90	90	71.26(3)	72.5180(10)	90	86.61(3)
V / Å^3	1264.5(5)	1863.5(7)	1670.1(6)	1276.9(4)	1763.6(7)	1720.39(11)	2926.3(6)	1281.8(5)
Z	4	6	4	4	2	2	4	2
Unique / I > 2σI	3679 / 3104	19833 / 18371	5060 / 4297	3406 / 3310	8397 / 7671	7924 / 6299	3349 / 1764	5833 / 4147
R_{int}	0.0987	0.0742	0.0247	0.0362	0.0262	0.0514	0.1222	0.0738
Parameters	179	1069	226	179	502	502	225	375
R_1 (all data / I > 2σI)	0.0720 / 0.0627	0.0618 / 0.0583	0.0580 / 0.0488	0.0433 / 0.0411	0.0385 / 0.0342	0.0545 / 0.0398	0.1287 / 0.0584	0.0916 / 0.0557
wR2 (all data / I > 2σI)	0.1734 / 0.1640	0.1629 / 0.1590	0.1408 / 0.1341	0.1133 / 0.1059	0.0841 / 0.0821	0.0973 / 0.0911	0.1459 / 0.1153	0.1489 / 0.1239
GooF	1.026	1.061	1.033	1.069	1.098	1.061	0.961	1.042
Residual max/min	0.574 / -0.367	0.428 / -0.347	0.431 / -0.355	0.358 / -0.223	0.470 / -1.760	0.414 / -0.349	0.398 / -0.631	0.946 / -1.093
Instrument	Synchrotron	Synchroton	Synchrotron	Synchrotron	Synchrotron	Bruker Apex II	Bruker Apex II	Synchrotron
T / K	100	100	100	100	100	123	123	100

Table 2: Crystallographic and refinement parameters for the structures of compounds **2** - **4**.

	[Co(4py3bz)$_2$]·3.5DMF (2·3.5DMF)	**[Zn(3py3bz)$_2$]·1.5H$_2$O (3Zn·1.5H$_2$O)**	**[Cd(3py3bz)$_2$]·1.5H$_2$O (3Cd·1.5H$_2$O)**	**[Co(4py4bz)$_2$]·16H$_2$O (4Co·16H$_2$O)**	**[Ni(4py4bz)$_2$]·7H$_2$O (4Ni·7H$_2$O)**
Formula [a]	$C_{38.5}H_{48.5}CoN_{9.5}O_{7.5}$	$C_{28}H_{27}N_6O_{5.5}Zn$	$C_{28}H_{27}CdN_6O_{5.5}$	$C_{28}H_{56}CoN_6O_{20}$	$C_{28}H_{38}N_6NiO_7$
M	823.30	600.92	647.95	855.71	693.35
Cell Setting	Monoclinic	Tetragonal	Tetragonal	Trigonal	Trigonal
Space Group	$P2_1/c$	$P4_12_12$	$P4_12_12$	$P3_121$	$P3_121$
a / Å	13.058(3)	12.344(2)	12.469(2)	14.780(2)	14.792(2)
b / Å	17.418(4)	12.344(2)	12.469(2)	14.780(2)	14.792(2)
c / Å	20.041(4)	17.575(4)	17.439(3)	19.179(4)	18.957(4)
α / º	90	90	90	90	90
β / º	108.21(3)	90	90	90	90
γ / º	90	90	90	120	120
V / Å^3	4329.8(17)	2678.0(9)	2711.3(9)	3628.3(12)	3592.2(14)
Z	4	4	4	3	3
Unique / I > 2σI	12186 / 9097	3833 / 3817	3908 / 3877	7002/4601	6951 / 6771
R_{int}	0.0478	0.0216	0.0148	0.6000	0.0306
Parameters	554	178	178	181	181
R_1 (all data / I > 2σI)	0.0887 / 0.1076	0.0362 / 0.0364	0.0270 / 0.0274	0.0747 / 0.0379	0.0279 / 0.0271
wR2 (all data / I > 2σI)	0.2908 / 0.3118	0.1189 / 0.1185	0.0663 / 0.0661	0.0922 / 0.0807	0.0762 / 0.0757
GooF	1.246	1.157	1.127	0.920	1.042
Residual max/min	1.113 / -0.729	0.493 / -1.434	1.057 / -1.454	0.137 / -0.408	0.264 / -0.332
Flack Parameter	-	0.032(3)	0.001(4)	0.033(8)	0.019(4)
Instrument	Synchrotron	Synchrotron	Synchrotron	Synchrotron	Synchrotron
T / K	100	100	100	100	100

(a) Formulae given correspond to those solely from X-ray data (including the use of SQUEEZE) rather than suggested by analytical data (see experimental section).