Copper(II) and cobalt(II) coordination polymers with bridging 1,2,4,5-benzenetetracarboxylate and *N*-methylimidazole: coordination number-determined sheet topology†

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Two new coordination polymers were synthesized under ambient conditions in water by combining a cobalt(II) or copper(II) metal salt with 1,2,4,5-benzenetetracarboxylate (BTEC) and *N*-methylimidazole (Meim), forming $Co_2(BTEC)(Meim)_4(H_2O)_4 \cdot H_2O$ (**1**) and $Cu_2(BTEC)(Meim)_4$ (**2**). Compounds **1** and **2** were characterized by X-ray crystallography, powder X-ray diffraction, TGA, FT-IR and elemental analysis. The crystal structures and 2D polymeric structures of compounds **1** and **2** are reported. Coordination polymer **1** crystallizes in the monoclinic space group $C2/c$. Coordination polymer **2** crystallizes in the triclinic space group $P\bar{1}$. Both **1** and **2** are made up of infinite sheets of BTEC ligands and metal ions. The sheets in **1** are puckered, giving an offset zigzag sheet topology, while the sheets in **2** are flat. Significant π–π stacking between Meim rings on adjacent sheets contributes to inter-sheet interactions in both **1** and **2**. While hydrogen bonding does not play a role in **2**, significant hydrogen bonding between sheets in **1** also stabilizes inter-sheet interactions.

Introduction

The design and synthesis of new supramolecular materials have garnered considerable interest.[1] Particularly interesting to inorganic chemists are coordination polymers (CPs), most often composed of transition metals and bridging ligands that form chains, sheets, and 3D networks.[2] Many CPs have zeolite-like structural properties such as large channels or void space, making them potential candidates for adsorption,[3,4] host–guest chemistry,[5] or catalysis.[6] Other CPs have been shown to have unusual magnetic[7] or non-linear optical properties.[8,9]

For the most part, researchers have focussed on altering the size, shape, and geometry of the ligands to attempt to control the structure of the CPs.[10] One particularly useful family of ligands that has been used to create a large number of CPs contain carboxylato functional groups. Ligands with at least two, and up to four carboxylates can bridge between metal ions to create 1D chains, 2D sheets, and 3D networks.[4,11–14]

Recently our laboratory has focussed on the simple aromatic carboxylates trimesitate (1,3,5-benzenetricarboxylate, TMA) and pyromellitate (1,2,4,5-benzenetetracarboxylate, BTEC). In particular, we are interested in using TMA or BTEC and non-bridging co-ligands with a variety of first-row transition metals to create CPs. Our goal is to probe the ability of these non-bridging co-ligands to influence the structures of the CPs. The synthesis of other mixed ligand CPs and their structures have been reported in the literature.[5,11,15]

TMA³⁻   BTEC⁴⁻   Him   Meim

We and others have synthesized CPs using TMA as a bridging ligand between transition metal ions.[4,12,13,16,17] We demonstrated that a small change in the co-ligand was critical in the stability of CPs comprised of copper(II), TMA, and either imidazole (Him) or *N*-methylimidazole (Meim).[16] In the case of Him, hydrogen bonding between 2D sheets stabilized the 3D structure. However, when the co-ligand was Meim, inter-sheet hydrogen bonding was disrupted, and the 3D structure was destabilized.[16]

The BTEC ligand has also been used to create CPs with a variety of metal ions. The species reported to date can be classified as bimetallic complexes,[18–21] 1D polymeric chains,[22–24] 2D polymeric sheets,[24–28] and 3D polymeric networks.[21,29] Several examples of BTEC complexes created with co-ligands (other than water) have been reported. Discrete binuclear complexes bridged by BTEC were prepared with L = 1,4,9-triisopropyl-[9]aneN₃, $[Cu_2(BTEC)L_2]$;[18] L = en, $[Ni_2(BTEC)L_2(H_2O)_6]$;[19] and L = *N*-(3-aminopropyl)propane-1,3-diamine, $[Cu_2(BTEC)L_2(H_2O)_2]$.[21] There have been numerous reports of 1D chain CPs with BTEC and aqua ligands, but only one example with a co-ligand, $[Cu_2(BTEC)(Him)_6(H_2O)_4]$.[22] Several structures have been reported where 2D sheets make up the CP, with L = 2,2′-bipy, $[Co_2(BTEC)L_2(H_2O)]$;[26] L = phen, $[Fe_2(BTEC)L_2]$;[27] and L = Him, $[Mn_2(BTEC)L_6]$.[28] Finally, one example of a 3D network CP with BTEC and L = dien has been reported, $[Cu_3(BTEC)L_3(H_2O)](ClO_4)_2$.[21]

Here we report the structures and characterization of two new CPs that are synthesized from identical ligand starting materials (BTEC and Meim) and differ only in the transition metals used [cobalt(II) and copper(II)]. The transition metals' coordination number and geometry are divergent in each CP, giving rise to strikingly different 2D structures. To our knowledge, there have been no reports of CPs that possess transition metal-dependent structural differences.
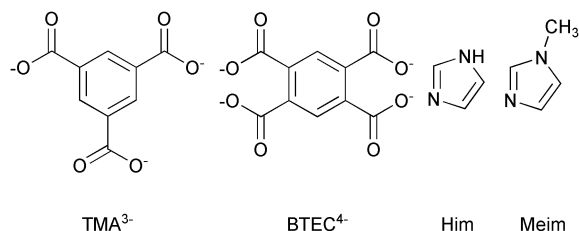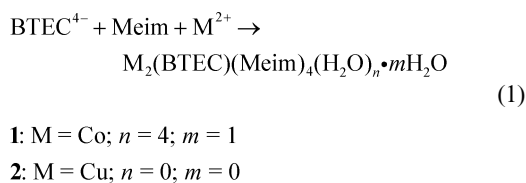
Results and discussion

The use of hydrothermal (solvothermal) reaction conditions wherein starting materials and solvent are combined in a

high pressure vessel and allowed to react at high temperature and pressure has become quite popular for the synthesis of CPs.[9,13,30] Our strategy for the synthesis of new CPs utilizes aqueous reaction conditions at room temperature and pressure. Our reactions generally conform to the following simple procedure: the pH of an aqueous solution of the carboxylic acid is adjusted to deprotonate the acid groups, followed by the addition of aqueous solutions of the co-ligand and the metal salt. Crystals suitable for X-ray crystallography can then be obtained *via* the slow evaporation of solvent.

The CPs reported here were synthesized using BTEC, Meim and either cobalt(II) or copper(II) according to eqn. (1). The pH of the aqueous BTEC solutions was adjusted to pH ≥ 7.0. Upon addition of the metal salt, some precipitation was observed and removed by filtration. Single crystals of $Co_2(BTEC)(Meim)_4$-$(H_2O)_4 \cdot H_2O$ (**1**) and $Cu_2(BTEC)(Meim)_4$ (**2**) were isolated by slow evaporation of filtered solutions. Both **1** and **2** are insoluble in water and common organic solvents.

$$BTEC^{4-} + Meim + M^{2+} \rightarrow$$
$$M_2(BTEC)(Meim)_4(H_2O)_n \cdot mH_2O$$

$$(1)$$

1: M = Co; *n* = 4; *m* = 1
2: M = Cu; *n* = 0; *m* = 0

$Co_2(BTEC)(Meim)_4(H_2O)_4 \cdot H_2O$ (1)

CP **1** was isolated as a crimson, crystalline solid and characterized by X-ray crystallography, powder X-ray diffraction (XRD), TGA, FT-IR and elemental analysis. A single crystal X-ray diffraction study of **1** revealed that it is made up of infinite sheets of cobalt atoms connected by BTEC ligands. The coordination environment around the cobalt(II) ions illustrated in Fig. 1 is six-coordinate, with a distorted octahedral geometry.
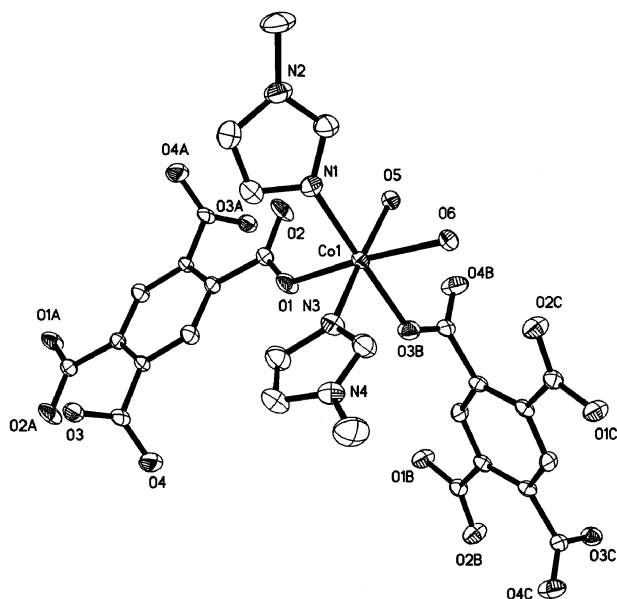
Fig. 1 Representation of a portion of CP **1** highlighting the asymmetric unit plus the symmetry-derived coordinated BTEC ligands (50% thermal ellipsoids, non-coordinated solvent water molecules and hydrogen atoms omitted for clarity).

Two carboxylato oxygen atoms, two aqua ligands and two Meim ligands in a *cis,cis,cis* arrangement coordinate to each cobalt atom. The *cis,cis,cis*-MA$_2$B$_2$C$_2$ octahedral isomer exists as an enantiomeric pair, and in the *C2/c* space group both enantiomers are present (the Λ-isomer is shown in Fig. 1).

Each carboxylato oxygen atom that coordinates to a cobalt atom is from a distinct, symmetry-related BTEC ion. Two of

Table 1 Selected bond lengths (Å) and angles (°) for CP **1**[a]

Co1–O1	2.093(3)	Co1–N1	2.097(3)
Co1–O3B[a]	2.086(3)	Co1–N3	2.104(3)
Co1–O5(w)	2.194(3)	Co1–O6(w)	2.169(3)
O1–Co1–O3B[a]	89.96(11)	O3B–Co1–O6[a]	83.35(10)
O1–Co1–N1[a]	91.19(12)	O5–Co1–O6	87.06(10)
O1–Co1–N3	90.66(11)	N1–Co1–N3	92.68(13)
O1–Co1–O5	89.96(10)	N1–Co1–O5	89.82(12)
O1–Co1–O6	172.64(11)	N1–Co1–O6	93.53(12)
O3B–Co1–N1	178.77(12)	N3–Co1–O5	177.41(11)
O3B–Co1–N3[a]	86.87(12)	N3–Co1–O6	92.03(12)
O3B–Co1–O5[a]	90.61(11)		

[a] Symmetry transformations used to generate equivalent atoms: $-x + 3/2$, $y - ½$, $-z + ½$.

the four carboxylato groups (O3–C13–O4 and O3A–C13A–O4A) on each BTEC ligand are twisted out of the plane of the aromatic ring by approximately 74°. The other two carboxylato groups (O1–C9–O2 and O1A–C9A–O2A) are nearly coplanar with the aromatic ring, having dihedrals of approximately 5°. The metal–ligand bond lengths and angles are all within expected limits for cobalt(II) complexes with carboxylates and *N*-heterocycles, and are summarized in Table 1 with hydrogen bond parameters in Table 2.[26]

Each BTEC ligand coordinates to four cobalt atoms, producing 2D sheets in the (100) plane. These sheets, shown in Fig. 2, are comprised of folded octagons. The corners of one octagon are made up of four BTEC ligands and four cobalt atoms. Each octagon is puckered out of the (100) plane, with the centers of the BTEC ligands generally in the plane of the sheets and the cobalt atoms bent above and below.
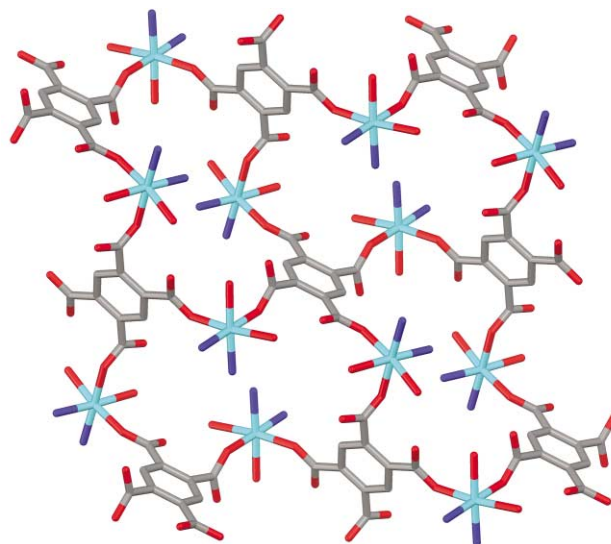
Fig. 2 Representation of a portion of the 2D sheets of CP **1** as viewed down the crystallographic *a* axis (hydrogen atoms, non-coordinated water molecules, and Meim rings omitted for clarity; carbon = gray; oxygen = red; nitrogen = blue; cobalt = light blue).

As illustrated in Fig. 3, the puckering produces a wave-like zigzag structure when the sheets are viewed from the side. The aromatic rings of the BTEC ligands are canted 60° out of the plane of the sheets. The diamond-shaped void space apparent in Fig. 3 is actually filled with the Meim ligands. The distance from crest to crest of the waves in CP **1** is 10.9 Å. The Co–Co distance between sheets is 5.7 Å, but the aqua ligand O atoms are separated by 2.8 Å, putting them within hydrogen bonding distance.

The buckling of the sheets in **1**, which creates the zigzag topology observed in Fig. 3, is due principally to the *cis* disposition of the carboxylato ligands and the octahedral coordination

Table 2 Hydrogen bonds (Å and °) in the crystal structure of CP **1**

D–H $\cdots$ A	d(D–H)	d(H $\cdots$ A)	d(D $\cdots$ A)	$\angle$(DHA)
O5–H5 $\cdots$ O2	0.85(2)	1.90(3)	2.714(4)	160(5)
O5–H5 $\cdots$ O3D[a]	0.85(2)	2.66(5)	3.043(4)	109(4)
O5–H5 $\cdots$ O4D[a]	0.85(2)	1.82(3)	2.633(4)	161(5)
O6–H6 $\cdots$ O2E[b]	0.84(2)	1.94(3)	2.775(4)	172(5)
O6–H6 $\cdots$ O3D[a]	0.84(2)	2.51(4)	2.829(4)	103(3)
O6–H6 $\cdots$ O5F[c]	0.85(2)	1.93(3)	2.770(4)	171(5)
O7–H7 $\cdots$ O6	0.85(2)	2.18(3)	3.023(5)	170(6)

Symmetry transformations used to generate equivalent atoms:[a] $-x + 3/2$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; [b] x, $-y + 1$, $z - \frac{1}{2}$; [c] $-x + 1$, $-y + 1$, $-z$.
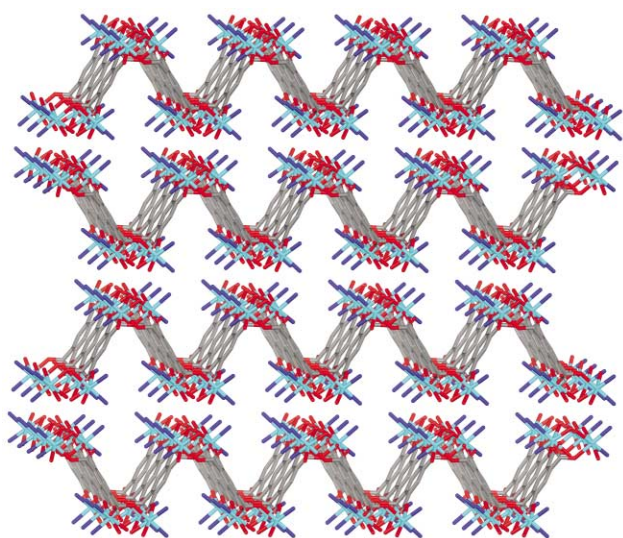
Fig. 3 Representation of CP **1** viewed along the crystallographic c axis illustrating the buckled sheets (hydrogen atoms, non-coordinated water molecules, and Meim rings omitted for clarity; carbon = gray; oxygen = red; nitrogen = blue; cobalt = light blue).

geometry around the cobalt atoms. CPs comprised of cobalt(II) and BTEC with *trans* carboxylato groups have flat 2D sheets made up of a rhombic grid of BTEC ligands and cobalt atoms.[24] Examples of CPs with wave-like structures have been reported where the sheets were packed such that the waves are in phase.[31] To our knowledge, **1** is the first example of a CP where the zigzag sheets are out of phase with each other.

Extensive hydrogen bonding occurs at the interface between sheets, which corresponds to the crests of the waves. Hydrogen bonding between aqua ligands and non-coordinating carboxylato oxygen atoms in the same sheet contributes to the overall topology of the sheets. Hydrogen bonding between aqua ligands on adjacent sheets contributes to inter-sheet attractions. One non-coordinated water molecule per formula unit is held by hydrogen bonding between sheets at the points of closest contact. Aqua ligand oxygen atom O6 is involved in hydrogen bonding with the non-coordinated solvent water.

The hydrogen bonding between sheets occurs where the crests of the wave-like sheets come together. The non-coordinating water molecules are encapsulated between sheets at these points. TGA analysis of **1** reveals that water molecules corresponding to approximately 12% of its mass are lost around 100 °C (see ESI†). The calculated mass loss for one uncoordinated water and two aqua ligands per formula unit is 11.5%. Heating the sample to higher temperatures leads to decomposition at around 300 °C.

A sample of **1** was ground into a powder and dried in a desiccator. The TGA of the dried sample of **1** is essentially unchanged, indicating that no water is lost when **1** is dried.† Furthermore, a comparison of the powder XRD of **1** before drying with the powder XRD of dried crystals indicates minimal changes occur upon drying.† Finally, a single crystal of **1** was dried in a desiccator for one week, and then analysed

Table 3 Selected bond lengths (Å) and angles (°) for CP **2**

Cu1–O1	1.9608(17)	Cu1–N1	1.998(2)
Cu2–O3	1.9734(16)	Cu2–N3	1.971(2)
O1–Cu1–N1	89.66(9)	O3–Cu2–N3	91.55(8)
O1A–Cu1–N1[a]	90.34(9)	O3–Cu2–N3A[b]	88.45(8)
O1–Cu1–O1A[a]	180.0	O3–Cu2–O3D[b]	180.0
N1–Cu1–N1A[a]	180.0	N3–Cu2–N3A[b]	180.0

Symmetry transformations used to generate equivalent atoms:[a] $-x$, $-y + 1$, $-z$; [b] $-x + 1$, $-y + 1$, $-z - 1$.

by single crystal X-ray crystallography. Unit cell parameters identical to those for **1** were obtained. Clearly, the uncoordinated water molecules in **1** are held in place very tightly *via* hydrogen bonding.

In addition to hydrogen bonding, inter-sheet contacts are strengthened by π–π interactions between Meim rings. Both unique Meim rings are parallel with their symmetry-related partners on adjacent sheets. The Meim ligand containing N3 and N4 has the closest contact with a centroid–centroid vector of 3.5 Å and an offset angle of 30°.‡ Compare for example the π–π interactions in the $Cu_3(TMA)_2(Him)_6(H_2O)$ complex, which has a centroid–centroid vector of 4.8 Å and an offset angle of 38°.[16] A slightly longer interaction is present between Meim rings containing N1 and N2 (3.9 Å, 42°). These π–π interactions are relatively strong, and presumably contribute to the structure and stability of **1**.

$Cu_2(BTEC)(Meim)_4$ (2)

CP **2** was synthesized in the same manner as CP **1** (see eqn. (1)). Deep blue, crystalline **2** was characterized by X-ray crystallography, TGA, powder XRD, FT-IR and elemental analysis. Like **1**, the polymeric structure of **2** is composed of 2D sheets. Two crystallographically independent copper atoms are each coordinated by a N_2O_2 ligand set. The coordination environment around the copper atoms shown in Fig. 4 is square planar, with two Meim and two carboxylato ligands in a *trans* disposition. The bond distances and angles around the copper atoms are typical for copper(II) coordinated by carboxylates and *N*-heterocycles and are summarized in Table 3.[16,32]

The sheets in **2** lie in the crystallographic (111) plane and are made up of BTEC ligands coordinated to copper(II) ions. The BTEC ligands coordinate in a μ_4-bridging mode, creating a flat topology with BTEC ligands on the corners and copper ions on the edges of a simple rhombic grid (Fig. 5). The carboxylato groups are twisted slightly out of the plane of the aromatic rings (dihedral angles of 35 and 60°), while the aromatic rings themselves are askew of the plane of the sheets by about 13°. The Meim ligands, which are canted out of the plane of the sheets by about 45°, occupy the space inside the 10 × 10 Å rhombic grid, precluding the inclusion of guest molecules.

Since the BTEC ligands coordinate *trans* to each other, the structure of the sheets in **2** are composed of four-sided rhombi

‡ The offset angle is defined as the angle between the normal of the Meim ring plane and the centroid–centroid vector.[36]
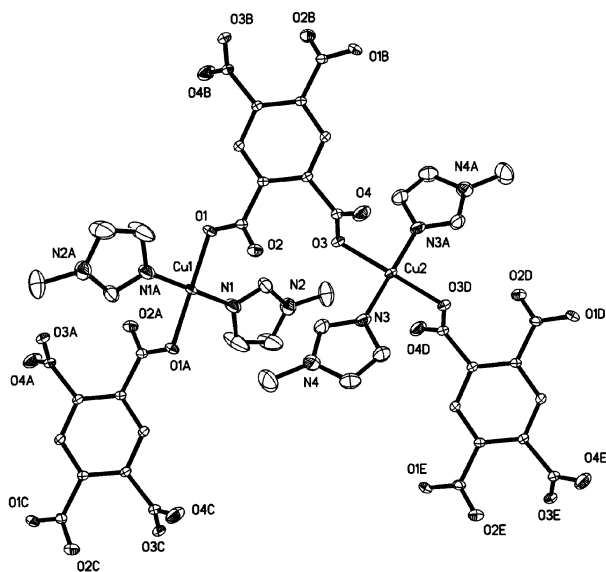
Fig. 4 Representation of a portion of CP **2** highlighting the asymmetric unit plus the symmetry derived BTEC and Meim ligands coordinated to the copper ions (50% thermal ellipsoids, hydrogen atoms omitted for clarity).
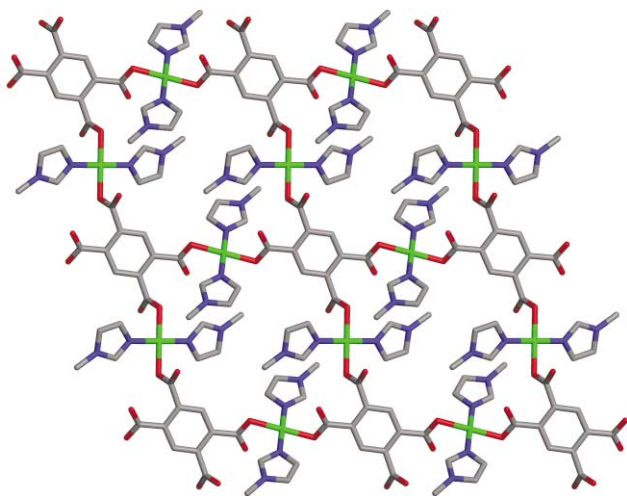
Fig. 5 Representation of a portion of the 2D sheets of CP **2** as viewed perpendicular to the (111) plane (hydrogen atoms omitted for clarity; carbon = gray; oxygen = red; nitrogen = blue; copper = green).

rather than the folded octagons that give rise to the zigzag sheets of **1**. As a consequence, the topology of the sheets in **2** is essentially flat. This difference between the topologies of the sheets in **1** and **2** is a direct result of the difference in coordination number and geometry of the metals. Fig. 6 shows the flat topology of the sheets in **2**. The sheet–sheet separation measured from copper atoms is about 8.8 Å. However, the
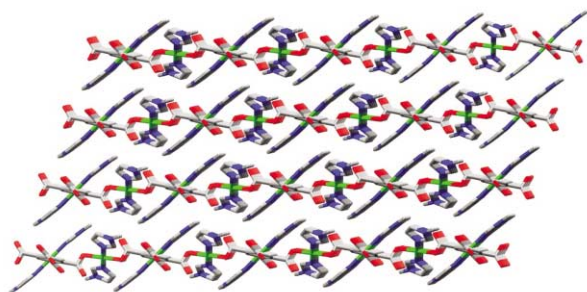
Fig. 6 Representation of CP **2** viewed parallel to the sheets and the (111) plane (hydrogen atoms omitted for clarity; carbon = gray; oxygen = red; nitrogen = blue; copper = green).

interdigitated Meim ligands are much closer to each other (*vide infra*).

Another difference between the structures of **1** and **2** is the absence of any water molecules, coordinated or uncoordinated, in **2**. The TGA of **2** supports this finding, with no mass change until decomposition occurs at about 250 °C.† As a consequence of the absence of water in CP **2**, there is no hydrogen bonding. However, π–π contacts between interdigitated Meim ligands on adjacent sheets does appear to contribute to inter-sheet interactions. A side view of the sheets of CP **2** in Fig. 6 illustrates the close contacts of the Meim rings on adjacent sheets. Surprisingly, only the Meim rings containing N3 and N4 are in close enough contact to interact through π–π bonding. The centroid–centroid distance for these Meim rings is about 3.8 Å and the offset angle is 23°. On the other hand, the centroid–centroid distance for the Meim rings containing N1 and N2 is greater than 5 Å. The inter-sheet π–π contacts between Meim ligands appear to be the only form of stabilization between sheets in CP **2**.

Conclusions

The flat sheet topology of CP **2** lies in stark contrast to the wave-like sheets in CP **1**. The difference in coordination environment between cobalt and copper in CPs **1** and **2**, respectively, is the primary reason the sheet topology is so divergent. Six-coordinate octahedral geometries are common for d^7 cobalt(II) complexes, whereas the Jahn–Teller distortion of d^9 copper(II) favors four-coordinate square planar or tetragonally distorted geometries.[33] This difference in coordination number and geometry between cobalt and copper leads to significant differences in polymeric structure. With BTEC as a bridging ligand and Meim as a co-ligand, the coordination geometry of the metal ion dictates the structure and topology of the 2D sheets. The differences between the structures of CPs **1** and **2** illustrate the remarkable influence that the coordination geometry of individual metal ions may have on the 2D and 3D structure of coordination polymers.

Experimental

General

All reagents were commercially available and used without further purification. Elemental analyses were carried out by Atlantic Microlabs of Norcross, GA. TGA experiments were performed on a Thermal Analyst 2000 TGA instrument under a helium atmosphere. The powder XRD data were collected on a Rigaku DMAX diffractometer at 295 K, operated at 40 kV and 30 mA, interfaced with an MDI databox and Jade 3.1 software, using Cu-Kα (λ = 1.5406 Å) radiation with a scan speed of 2° min^{-1}. The IR spectra were recorded on a Nicolet Nexus 470 FT-IR at room temperature using the KBr pellet technique.

Synthesis

The synthetic methods used to obtain large single-crystal samples of the compounds, including their initial characterization, are described here. All reactions and purification steps were performed under aerobic conditions at room temperature.

Co_2(BTEC)(Meim)$_4$(H_2O)$_4$·H_2O (1). About 5 mmol (1.27 g) of H$_4$BTEC was slowly added to a 20 mL aqueous solution of NaOH (0.80 g, 20 mmol) with stirring until pH ≥ 7.0. Cobalt(II) sulfate hydrate (2.81 g, 10 mmol) was dissolved in 20 mL of water and added to the BTEC solution. Meim (1.64 g, 20 mmol) was then slowly added with stirring until the pink solution turned dark red. The solution was filtered and allowed to stand at room temperature. Crimson single crystals of Co_2(BTEC)(Meim)$_4$(H_2O)$_4$·H_2O (**1**) were obtained after six days (1.13 g, 29%). Found: C, 39.14; H, 4.57; N, 13.90.

Table 4 Crystallographic data and refinement details for **1** and **2**

	1	2
Empirical formula	$C_{13}H_{18}CoN_4O_{6.5}$	$C_{13}H_{13}CuN_4O_4$
Formula weight	393.24	352.81
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a/Å	24.148(10)	8.847(2)
b/Å	10.908(6)	8.985(2)
c/Å	12.942(5)	10.3302(17)
α/°	90	67.817(12)
β/°	107.67(2)	82.839(17)
γ/°	90	75.60(2)
V/Å³	3248(2)	736.0(3)
Z	8	2
μ/mm⁻¹	1.099	1.507
$F(000)$	1624	360
Crystal size/mm	$0.40 \times 0.18 \times 0.08$	$0.48 \times 0.32 \times 0.22$
Reflections collected	2963	3534
Independent reflections (R_{int})	2829 (0.0481)	2934 (0.0306)
Data/restraints/parameters	2829/10/243	2934/0/205
Final R [$I > 2\sigma(I)$]		
$R1$	0.0447	0.0402
w$R2$	0.1061	0.1026
R (all data)		
$R1$	0.0617	0.0517
w$R2$	0.1160	0.1108

$C_{13}H_{18}CoN_4O_{6.5}$ requires C, 39.71; H, 4.61; N, 14.99%. ν_{max}/cm⁻¹ (KBr) 3327s, 3136s, 1586s, 1538w, 1484m, 1417s, 1379s, 1321m, 1283m, 1234s, 1138m, 1101s, 1028w, 945m, 829w, 761s, 736w, 675w, 660 m, 617s, 582m, 418w.

Cu₂(BTEC)(Meim)₄ (2). About 5 mmol (1.27 g) of H₄BTEC was slowly added to a 20 mL aqueous solution of NaOH (0.80 g, 20 mmol) with stirring until pH ≥ 8.0. Copper(II) sulfate hydrate (2.52 g, 10 mmol) was dissolved in 20 mL of water and added to the BTEC solution, immediately resulting in the formation of a light blue precipitate. Meim (1.64 g, 20 mmol) was then slowly added with stirring until most of the precipitate dissolved and the color of the solution turned dark blue. The solution was filtered and allowed to stand at the room temperature. Deep blue single crystals of Cu₂(BTEC)(Meim)₄ (**2**) were obtained after one week (0.98 g, 28%). Found: C, 44.83; H, 3.69; N, 15.82. $C_{13}H_{13}CuN_4O_4$ requires C, 44.26; H, 3.71; N, 15.88%. ν_{max}/cm⁻¹ (KBr) 3428s, 1603s, 1489w, 1387m, 1353m, 1284w, 1239w, 1010s, 956w, 867w, 820w, 762w, 654w, 619w, 554w.

X-Ray crystallography

The crystal data and data collection parameters for **1** and **2** are summarized in Table 4. The intensity data for both crystals were collected on a Bruker P4 diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation in the ω–2θ scanning mode at 295(2) K. The data were corrected for Lorentz and polarization effects as well as absorption. All structures were solved by the Patterson method followed by Fourier synthesis. Structure refinement was carried out by full-matrix least-squares procedures using the SHELXTL program package.[34] H atoms were located in a difference Fourier map, and coordinates and thermal parameters were fixed during structure refinement. All non-hydrogen atoms were refined anisotropically. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[35]

CCDC reference numbers 191132 and 191133.

See http://www.rsc.org/suppdata/dt/b2/b207559h/ for crystallographic data in CIF or other electronic format.

References

1 J.-M. Lehn, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4763–4768; J.-M. Lehn, *Science*, 2002, **295**, 2400–2403; D. N. Reinhoudt and M. Crego-Calama, *Science*, 2002, **295**, 2403–2407; O. Ikkala and G. ten Brinke, *Science*, 2002, **295**, 2407–2409; M. D. Hollingsworth, *Science*, 2002, **295**, 2410–2413; T. Kato, *Science*, 2002, **295**, 2414–2418; G. M. Whitesides and B. Grzybowski, *Science*, 2002, **295**, 2418–2421.
2 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629–1658; M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319–330.
3 A. J. Fletcher, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, C. J. Kepert and K. M. Thomas, *J. Am. Chem. Soc.*, 2001, **123**, 10001–10011; X. Wang, L. Liu and A. J. Jacobson, *J. Am. Chem. Soc.*, 2002, **124**, 7812–7820; M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469–472.
4 S. S. Chui, S. M. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148–1150.
5 F. M. Tabellion, S. R. Seidel, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2001, **123**, 11982–11990.
6 M. Abrantes, A. Valente, M. Pillinger, I. S. Goncalves, J. Rocha and C. C. Romao, *J. Catal.*, 2002, **209**, 237–244.
7 J. C. Noveron, M. S. Lah, R. E. Del Sesto, A. M. Arif, J. S. Miller and P. J. Stang, *J. Am. Chem. Soc.*, 2002, **124**, 6613–6625; H. Kou, J. Tang, D. Liao, S. Gao, P. Cheng, Z. Jiang, S. Yan, G. Wang, B. Chansou and J. P. Tuchagues, *Inorg. Chem.*, 2001, **40**, 4839–4844; H. Kou, S. Gao, J. Zhang, G. Wen, G. Su, R. K. Zheng and X. X. Zhang, *J. Am. Chem. Soc.*, 2001, **123**, 11809–11810; E. Coronado, J. R. Galan-Mascaros, C. J. Gomez-Garcia and V. Laukhin, *Nature*, 2000, **408**, 447–449.
8 W. B. Lin, Z. Y. Wang and L. Ma, *J. Am. Chem. Soc.*, 1999, **121**, 11249–11250.
9 R. E. Sykora, K. M. Ok, P. S. Halasyamani and T. E. Albrecht-Schmitt, *J. Am. Chem. Soc.*, 2002, **124**, 1951–1957.
10 F. A. Cotton, C. Lin and C. A. Murillo, *Inorg. Chem.*, 2001, **40**, 5886–5889; P. Ayyappan, O. R. Evans and W. Lin, *Inorg. Chem.*, 2002, **41**, 3328–3330; H. K. Chae, M. Eddaoudi, J. Kim, S. I. Hauck, J. F. Hartwig, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 11482–11483.
11 S. M. Lo, S. S. Chui, L. Shek, Z. Lin, X. Zhan, G. Wen and I. D. Williams, *J. Am. Chem. Soc.*, 2000, **122**, 6293–6294.
12 H. J. Choi and M. P. Suh, *J. Am. Chem. Soc.*, 1998, **120**, 10622–10628.
13 M. J. Plater, M. R. S. Foreman, E. Coronado, C. J. Gomez-Garcia and A. M. Z. Slawin, *J. Chem. Soc., Dalton Trans.*, 1999, 4209–4216.
14 B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021–1023; J. Kim, B. L. Chen, T. M. Reineke, H. L. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239–8247.
15 Z. Shi, S. Feng, Y. Sun and J. Hua, *Inorg. Chem.*, 2001, **40**, 5312–5313; J. J. Bodwin and V. L. Pecoraro, *Inorg. Chem.*, 2000, **39**,

3434–3435; J. Y. Lu, K. A. Runnels and C. Norman, *Inorg. Chem.*, 2001, **40**, 4516–4517; R. Kitaura, K. Fujimoto, S. Noro, M. Kondo and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2002, **41**, 133–135; S. A. Bourne, J. J. Lu, A. Mondal, B. Moulton and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2001, **40**, 2111–2113; H. J. Choi, T. S. Lee and M. P. Suh, *Angew. Chem., Int. Ed.*, 1999, **38**, 1405–1408.

16 D. Cheng, M. A. Khan and R. P. Houser, *Inorg. Chem.*, 2001, **40**, 6858–6859.

17 O. M. Yaghi, H. L. Li and T. L. Groy, *J. Am. Chem. Soc.*, 1996, **118**, 9096–9101.

18 P. Chaudhuri, K. Oder, K. Wieghardt, S. Gehring, W. Haase, B. Nuber and J. Weiss, *J. Am. Chem. Soc.*, 1988, **110**, 3657–3658.

19 D. Poleti, D. R. Stojakovic, B. V. Prelesnik and R. M. Herak, *Acta Crystallogr., Sect. C*, 1988, **44**, 242–245.

20 F. D. Rochon and G. Massarweh, *Inorg. Chim. Acta*, 2000, **304**, 190–198; D. Cheng, Y. Zheng, J. Lin, D. Xu and Y. Xu, *Acta Crystallogr., Sect. C*, 2000, **56**, 523–524.

21 J. Zou, Q. Liu, Z. Xu, X. You and X. Huang, *Polyhedron*, 1998, **17**, 1863–1869.

22 D. Cheng, C. Feng, M. Hu, Y. Zheng, D. Xu and Y. Xu, *J. Coord. Chem.*, 2001, **52**, 245–251.

23 D. Poleti and L. Karanovic, *Acta Crystallogr., Sect. C*, 1989, **45**, 1716–1718; R. Murugavel, D. Krishnamurthy and M. Sathiyendiran, *J. Chem. Soc., Dalton Trans.*, 2002, 34–39.

24 D. Cheng, M. A. Khan and R. P. Houser, *Cryst. Growth Des.*, 2002, **2**, 415–420.

25 C. Robl, *Z. Anorg. Allg. Chem.*, 1987, **554**, 79–86; C. Robl, *Z. Naturforsch., Teil B*, 1988, **43**, 993–997.

26 M. J. Plater, M. R. S. J. Foreman, R. A. Howie, J. M. S. Skakle and A. M. Z. Slawin, *Inorg. Chim. Acta*, 2001, **315**, 126–132.

27 D. Chu, J. Xu, L. Duan, T. Wang, A. Tang and L. Ye, *Eur. J. Inorg. Chem.*, 2001, 1135–1137.

28 M. Hu, D. Cheng, J. Liu and D. Xu, *J. Coord. Chem.*, 2001, **53**, 7–13.

29 F. Jaber, F. Charbonnier and R. Faure, *J. Chem. Crystallogr.*, 1997, **27**, 397–400; H. Kumagai, C. J. Kepert and M. Kurmoo, *Inorg. Chem.*, 2002, **41**, 3410–3422.

30 K. Y. Choi, K. M. Chun and I. H. Suh, *Polyhedron*, 2001, **20**, 57–65; R. C. Finn, R. Lam, J. E. Greedan and J. Zubieta, *Inorg. Chem.*, 2001, **40**, 3745–3754; P. Ayyappan, O. R. Evans and W. B. Lin, *Inorg. Chem.*, 2002, **41**, 3328–3330.

31 Y. Liang, M. Hong, W. Su, R. Cao and W. Zhang, *Inorg. Chem.*, 2001, **40**, 4574–4582; Y. J. Zhao, M. C. Hong, D. F. Sun and R. Cao, *J. Chem. Soc., Dalton Trans.*, 2002, 1354–1357.

32 M. Melnik, *Coord. Chem. Rev.*, 1982, **42**, 259–293.

33 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, New York, 1988.

34 G. M. Sheldrick, SHELXTL, Version 5.1, Bruker AXS, 1997.

35 T. Hahn, in *International Tables for X-Ray Crystallography*, Dordrecht, The Netherlands, 1989.

36 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885–3896.