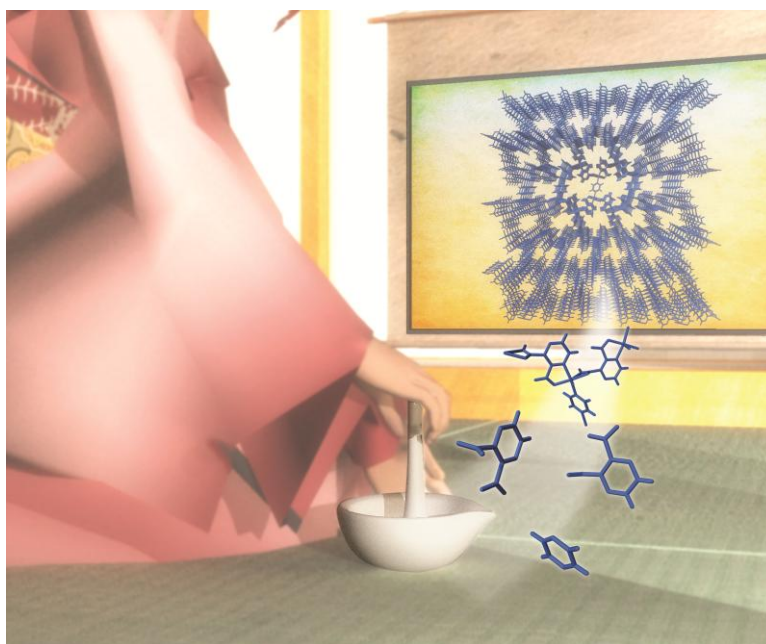


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PAPER

Supramolecular isomers of metal–organic frameworks: the role of a new mixed donor imidazolate-carboxylate tetradentate ligand†

Victoria J. Richards, Stephen P. Argent, Adam Kewley, Alexander J. Blake, William Lewis and Neil R. Champness*

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Five new metal–organic frameworks prepared from the ligand 5-bis(3-(1-imidazolyl)propylcarbamoyl)terephthalate (bipta^{2-}) and transition metal salts, Zn^{2+} (**1**), Co^{2+} (**2**), Mn^{2+} (**3**, **4**) and Cu^{2+} (**5**), are reported. Single crystal X-ray studies reveal that the bipta^{2-} ligand acts as a tetradentate ligand and combines with four-coordinate cationic metal nodes to give four-connected framework structures. Whilst reaction of bipta^{2-} with $\text{Zn}(\text{II})$ gives rise to a framework of diamondoid topology **1**, the analogous frameworks with $\text{Co}(\text{II})$, $\text{Mn}(\text{II})$ and $\text{Cu}(\text{II})$ afford frameworks that incorporate square-planar nodes. Whereas **2** and **5** form frameworks of $\text{Cd}(\text{SO}_4)$ (**cds**) and square 4^4 nets (**sql**), respectively, reaction of $\text{Mn}(\text{II})$ with bipta^{2-} forms two supramolecular isomers of topology **cds** for **3** and **sql** for **4**.

Introduction

Metal–organic frameworks (MOFs) represent one of the most topical fields of chemistry and materials science.^{1–4} The interest in the field stems from the application of MOFs in various fields ranging from gas storage³ to magnetic materials.⁴ All of these applications rely on the simple principle that the structures of MOFs position molecular components in a regular arrangement in three-dimensional space.¹

For these applications to be developed and honed, the synthesis of MOFs has to be reliable and to some extent predictable. In this regard an interesting aspect of studying MOFs, or coordination polymers,⁵ arises from their ability to form isomeric framework arrangements from the same component building-blocks.^{6,7} Such MOFs are known as supramolecular isomers,⁶ although other terms, including topological or framework isomers, have been used.⁷ Notable examples of supramolecular isomers have been reported for systems where the ligands offer multiple donor types, acting as multi-modal components of the framework.⁸ Indeed, the use of building-blocks that are able to adopt a variety of ligand coordination modes or a degree of flexibility can lead to a highly complex array of possible structural arrangements encouraging the formation of supramolecular isomers. Our studies of mixed-donor systems have demonstrated that the combination of different donors within the same ligand can facilitate the formation of alternative structural arrangements in contrast to simple combinations of more than one ligand.⁹

In this study we have focussed on a new ligand system, 5-bis(3-(1-imidazolyl)propylcarbamoyl)terephthalic acid (biptaH_2), that contains two carboxylic acid and two imidazole donors. The ligand incorporates both carboxylate donors, which have been widely exploited in MOF chemistry,¹⁰ and imidazolate donors, which have been used to synthesise zeolitic imidazolate frameworks (ZIFs), which constitute a new class of MOF-like materials.¹¹ Our studies demonstrate the formation of supramolecular isomers and illustrate the level of complexity involved in the design and synthesis of MOF materials.

Results and discussion

The ligand biptaH_2 was prepared in a single-step procedure by reaction of 1,2,4,5-benzene-tetracarboxylicdianhydride with 1-(3-aminopropyl)imidazole in *N,N*-dimethylformamide at 90 °C over 24 h. Although under some conditions the reaction of the anhydride group with an amine leads to the formation of an imide,¹² the strained anhydride rings of 1,2,4,5-benzene-tetracarboxylicdianhydride lead to the stabilisation of the amic acid species.¹³ The structure of the ligand, biptaH_2 was confirmed by single-crystal X-ray diffraction studies (Fig. 1), which revealed that the ligand crystallises in a zwitterionic form, with protonated imidazole groups and deprotonated carboxylates.

Reaction of biptaH_2 with metal salts led to the formation of MOF materials. Single crystals of $[\text{M}(\text{bipta})(\text{H}_2\text{O})_n]_\infty$, where $\text{M} = \text{Zn}^{2+}$ (**1**), Co^{2+} (**2**), Mn^{2+} (**3**, **4**), were grown by slow solvent diffusion between an upper layer of $\text{M}(\text{NO}_3)_2$ in MeOH or MeCN and a lower layer of biptaH_2 in H_2O . For **1** and **2**, single-crystal X-ray diffraction experiments demonstrated a single phase for each system regardless of solvent conditions, whilst for $\text{Mn}(\text{II})$, solvent-induced supramolecular isomerism is indicated by the observation of two distinct phases, **3** and **4**. Single

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crystals of $[\text{Cu}(\text{bipta})(\text{H}_2\text{O})_{18}]_{\infty}$ (**5**) were grown from the slow diffusion of $\text{Cu}(\text{NO}_3)_2$ in H_2O into a solution of biptaH_2 in H_2O .

A single-crystal structural determination on $[\text{Zn}(\text{bipta})]_{\infty}$ (**1**) reveals the formation of a three-dimensional framework. Each $\text{Zn}(\text{II})$ cation is tetrahedrally coordinated by four bipta^{2-} ligands *via* two carboxylate and two imidazole donors (Fig. 2a, Table 1), whilst each bipta^{2-} is coordinated *via* all four of its potential binding sites. Topological analysis of the framework structure reveals a binodal network of 6^6 **dia** topology,¹⁴ which exhibits threefold interpenetration (Fig. 3a). A large number of interpenetrated diamond nets are known¹⁵ including triply-interpenetrated examples based on zinc(II) cations.¹⁶

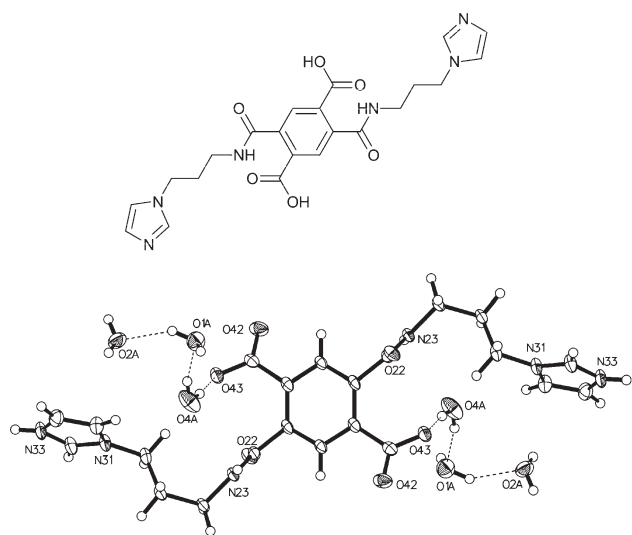


Fig. 1 The ligand biptaH_2 and a view of the crystal structure of the uncoordinated ligand. Only one disorder component of the water molecules is shown. Displacement ellipsoids are drawn at the 50% probability level.

The single-crystal X-ray structure determination of $\{[\text{Co}(\text{bipta})(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\}_{\infty}$ (**2**) reveals that each $\text{Co}(\text{II})$ cation occupies an octahedral coordination sphere comprising four bipta^{2-} ligands, which coordinate *via* two carboxylate and two imidazole donors, in addition to two water molecules (Fig. 2b, Table 1). The coordinated H_2O ligands form hydrogen bonding interactions to neighbouring carboxylate groups (Table 2). Topological analysis of the framework formed by **2**, considering only coordination bonds, reveals an overall $6^5 8$ **cds** topology¹⁴ (Fig. 3).

Interestingly, the X-ray diffraction studies of single crystals grown from the reaction of $\text{Mn}(\text{NO}_3)_2$ with biptaH_2 in either MeOH (**3**) or MeCN (**4**) reveal coordination frameworks of formula $\{[\text{Mn}(\text{bipta})(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\}_{\infty}$, but the two networks are topologically distinct. A structure determination on **3** reveals a three-dimensional framework, which is topologically equivalent to **2**, *i.e.*, it adopts a $6^5 8$ **cds** topology¹⁴ (Table 1), and similarly includes four uncoordinated solvent water molecules per metal ion. A structure determination on **4** reveals a similar $\text{Mn}(\text{II})$ coordination environment to that of **3**, as well as the same stoichiometry for the solvent (Fig. 2c, Table 1). However, the three-dimensional connectivity is drastically different, in that **4** is composed of two-dimensional networks of 4^4 **sql** topology¹⁴ (Fig. 3c). Thus, frameworks **3** and **4** can be considered to be supramolecular, or topological, isomers.^{6,7} Inspection of the extended structures and in particular the hydrogen-bonding interactions observed in **3** and **4** reveals further details of the supramolecular isomerism observed. Whereas **3** forms a three-dimensional structure based upon coordinate interactions, **4** forms two-dimensional sheets, which stack in an eclipsed undulating conformation in the crystallographic ab plane such that channels are formed within the structure that run parallel to the c axis. In **3** the solvent water molecules lie in the channels of the framework in close proximity to the $\text{Mn}(\text{II})$ coordination spheres; **O2A** forms hydrogen bonding interactions with both coordinated water ligand **O1A** and coordinated carboxylate oxygen atom

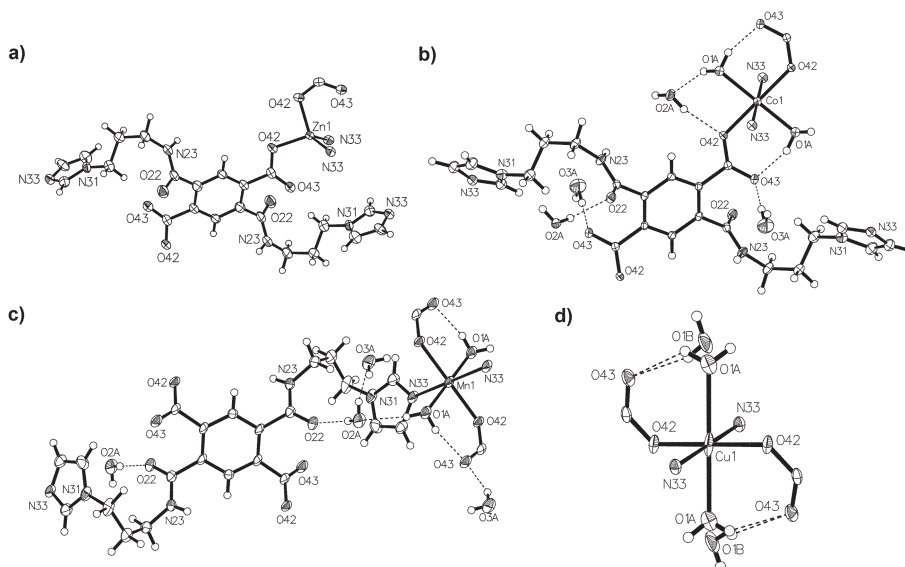


Fig. 2 Views of the metal coordination environments adopted by (a) **1**, (b) **2**, (c) **4** and (d) **5**. Displacement ellipsoids are drawn at the 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for **1–5**

| 1 | | 2 | | 3 | |
|--|------------|---------------------------|------------|--------------------------|------------|
| Zn1–O42 | 1.9878(13) | Co1–O42 | 2.1555(15) | Mn1–O42 | 2.2090(16) |
| Zn1–N33 ^a | 2.0045(15) | Co1–N33 ^d | 2.105(2) | Mn1–N33 | 2.218(2) |
| O42–Zn1–N33 ^b | 114.92(7) | Co1–O1A | 2.1339(17) | Mn1–O1A | 2.2177(19) |
| O42–Zn1–N33 ^c | 110.44(7) | O42–Co1–N33 ^d | 85.93(7) | O42–Mn1–N33 | 85.53(7) |
| N33 ^c –Zn1–N33 ^b | 112.16(9) | O42–Co1–N33 ^e | 94.07(7) | O42–Mn1–N33 ^g | 94.47(7) |
| O42 ^a –Zn1–O42 | 92.66(8) | O1A–Co1–N33 ^e | 87.58(8) | O1A–Mn1–N33 ^g | 87.44(8) |
| | | O1A–Co1–N33 ^d | 92.42(8) | O1A–Mn1–N33 | 92.56(8) |
| | | O42–Co1–O1A | 89.55(6) | O42–Mn1–O1A | 88.67(7) |
| | | O42–Co1–O1A ^f | 90.45(6) | O42–Mn1–O1A ^g | 91.33(7) |
| 4 | | 5 | | | |
| Mn1–O42 ^h | 2.214(2) | Cu1–O42 | 1.985(2) | | |
| Mn1–N33 | 2.237(3) | Cu1–N33 ^k | 1.964(3) | | |
| Mn1–O1A | 2.219(3) | Cu1–O1A | 2.45(2) | | |
| O42 ^l –Mn1–N33 | 89.79(10) | O42–Cu1–N33 ^k | 89.32(11) | | |
| O42 ^h –Mn1–N33 | 90.21(10) | O42–Cu1–N33 ^l | 90.68(11) | | |
| O1A–Mn1–N33 ^l | 87.69(10) | O1A–Cu1–N33 ^k | 86.9(2) | | |
| O1A–Mn1–N33 | 92.31(10) | O1A–Cu1–N33 ^l | 93.1(2) | | |
| O42 ^l –Mn1–O1A | 89.87(9) | O42 ^m –Cu1–O1A | 81.1(2) | | |
| O42 ^h –Mn1–O1A | 90.13(9) | O42–Cu1–O1A | 98.9(2) | | |

^a $1-x, 3/2-y, z$. ^b $5/4-x, 5/4-y, 7/4-z$. ^c $1/4+x, -1/4+y, 7/4-z$. ^d $1-x, -1/2+y, 1/2-z$. ^e $1+x, 1/2-y, 1/2+z$. ^f $2-x, -y, 1-z$. ^g $1-x, 2-y, 2-z$. ^h $1+x, 1+y, z$. ⁱ $-x, -y, 1-z$. ^j $1-x, 1-y, 1-z$. ^k $1-x, -y, -z$. ^l $-1+x, y, z$. ^m $-y, -x, -z$.

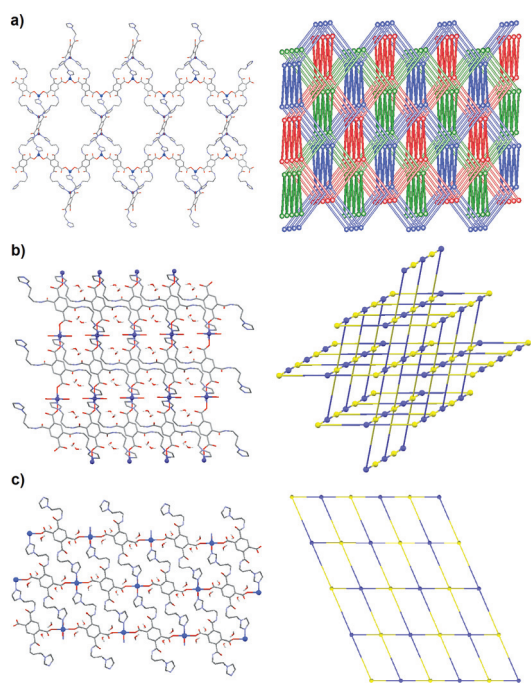


Fig. 3 Left: Views of the crystal structures of (a) **1**, (b) **2**, **3** and (c) **4** showing the extended networks formed within each given framework. Right: the corresponding topological representations showing (a) three triply interpenetrating nets of 6^6 dia topology within **1**, (b) $6^5 8$ cds topology of **2** and **3** and (c) 4^4 sql topology of **4** and **5**; blue = metal centre, yellow = ligand node, water ligands have been omitted for clarity.

O42, whilst O3A donates a hydrogen bond to the uncoordinated carboxylate oxygen atom O43 (Fig. 4a, Table 2). In **4** the solvent molecules are positioned between the sheets of the framework

such that water molecules O2A and O3A participate in an inter-sheet hydrogen bonding bridge between the carbamoyl oxygen atom O22 of a primary sheet and the uncoordinated carboxylate oxygen atom O43 of a symmetry-related secondary sheet. O2A provides a further intra-sheet bridge as a result of hydrogen bonding interactions with both a carbamoyl oxygen atom O22 and a water ligand present within a single sheet (Fig. 4b, Table 2).

A structure determination on $\{[\text{Cu}(\text{bipta})(\text{H}_2\text{O})_2] \cdot 16\text{H}_2\text{O}\}_\infty$ (**5**) demonstrates that the framework adopts the same topology as that of **4**, namely a two-dimensional network of 4^4 sql topology. The Cu(II) coordination sphere is best viewed as having a Jahn–Teller distorted octahedral geometry with water molecules occupying the axial sites (Table 1). However, the coordination sphere is disordered in the axial sites with both coordinated water ligands (0.57 occupancy) and uncoordinated water ligands (0.43 occupancy) (Fig. 2d). Thus the two disordered arrangements of the Cu(II) coordination sphere varies from distorted octahedral to square-planar. This disorder has no impact on the topology of the coordination polymer framework. Additionally, sixteen solvent water molecules per metal ion are present in the structure of **5**, in comparison to the four per metal ion observed in **4**. These water molecules participate in a complex network of inter- and intra-sheet hydrogen-bonding interactions.

Powder X-ray diffraction (PXRD) analyses of **1** and **2** confirmed that the bulk samples adopt the same phases as those of their respective single crystals (see ESI†). The single crystal structure determination of **1** was unable to define the nature of the guest molecules, due to significant disorder, and elemental analysis did not give an unambiguous determination of the solvent present. However, it is important to note that the framework structure of **1** is unambiguously confirmed by the PXRD studies.

PXRD studies of bulk samples of **3** and **4** were used to determine whether the reaction conditions used, particularly the

solvent used, would favour a particular isomer. Comparison of the experimental pattern for **3** with the simulated patterns of both isomers shows that the bulk sample of **3** is predominantly composed of the 6^38 **cds** framework, the same phase observed during single crystal studies (Fig. 5). However, peaks of significant intensity at 31.0° and 39.0° in 2θ indicate the possible presence of an additional phase. The nature of this phase is unclear, although it should be noted that in addition to the **cds** and **sql** topologies reported herein, square planar nodes are known to assemble into 6^48^2 **nbo**¹⁷ and 4^28^4 **lvt**¹⁸ nets. As the purity of the sample has been confirmed by elemental analysis, it is proposed that a third or fourth phase possessing these alternative topologies, although unobserved during single crystal studies, may be present within the bulk sample of **3**. PXRD analysis of **4** indicates that the bulk sample is largely composed of a mixture of the **sql** and **cds** isomers (Fig. 6). Ambiguity over the assignments of certain peaks at high 2θ indicates that **4** may also contain additional phases of **nbo** or **lvt** topology unobserved in the single crystal studies.

Conclusions

In this study we demonstrate the exploitation of a new mixed carboxylate–imidazolate ligand and show its potential to form a range of framework structures that combine the tetradentate binding mode of bipta^{2-} with tetra-coordinate metal centres. Whereas Zn(II) adopts a tetrahedral coordination sphere in the **dia** structure of **1**, Co(II), Mn(II) and Cu(II) all adopt octahedral environments, coordinating two water ligands in addition to four bipta^{2-} ligands, and thus forming square-planar framework nodes. Our study reveals a highly unusual example of supramolecular isomerism in the two Mn(II) MOFs, **3** and **4**, which adopt **cds** and **sql** structures, respectively. Interestingly, powder X-ray diffraction studies show that bulk samples contain both isomers, as well as an additional phase.

Although the formation of supramolecular isomers is theoretically possible for many node types in framework structures, the characterisation of such isomeric structures remains unusual. Indeed, powder X-ray diffraction analysis can often reveal the presence of additional phases within the bulk samples of MOF

Table 2 Selected hydrogen bond lengths (Å) and angles ($^\circ$) for **2–5**

| | D–H...A | d(D–H) | d(H...A) | d(D...A) | <(DHA) |
|----------|-----------------------------|---------------|---------------|---------------|---------|
| 2 | N23–H23...O22 ^a | 0.88 | 2.19 | 2.978(3) | 148.8 |
| | O1A–H1AA...O43 | 0.856 (18) | 1.803 (19) | 2.610(2) | 156(3) |
| | O1A–H1AB...O2A ^b | 0.825 (17) | 1.87(2) | 2.612(3) | 148(3) |
| | O2A–H2AA...O42 ^c | 0.827 (18) | 2.004 (19) | 2.806(3) | 163(4) |
| | O2A–H2AB...O22 | 0.841 (18) | 1.97(3) | 2.725(3) | 149(4) |
| | O3A–H3AA...O43 ^d | 0.924 (18) | 1.906 (19) | 2.825(3) | 173(4) |
| 3 | O3A–H3AB...O2A ^e | 0.927 (18) | 2.38(3) | 3.077(4) | 131(3) |
| | N23–H23...O22 ^f | 0.88 | 2.18 | 2.982(3) | 151 |
| | O1A–H1AB...O43 | 0.824 (18) | 1.88(2) | 2.640(3) | 152(4) |
| | O1A–H1AA...O2A ^g | 0.813 (18) | 1.92(2) | 2.596(3) | 140(3) |
| | O2A–H2AA...O42 ^h | 0.823 (19) | 2.09(2) | 2.857(3) | 154(4) |
| | O2A–H2AB...O22 ⁱ | 0.821 (19) | 2.07(4) | 2.756(3) | 141(6) |
| 4 | O3A–H3AA...O43 ^j | 0.923 (19) | 1.93(2) | 2.826(4) | 164(5) |
| | O3A–H3AB...O2A ^e | 0.92(2) | 2.41(4) | 3.055(5) | 127(4) |
| | O1A–H1AA...O43 ^k | 0.825 (18) | 1.98(2) | 2.760(4) | 159(4) |
| | O1A–H1AB...O2A ^l | 0.826 (18) | 1.991 (18) | 2.811(4) | 172(4) |
| | O2A–H2AA...O3A ^k | 0.829 (18) | 2.005 (19) | 2.803(4) | 161(4) |
| | O2A–H2AB...O22 | 0.817 (18) | 2.01(2) | 2.814(4) | 166(5) |
| 5 | O3A–H3AA...O42 | 0.819 (18) | 2.38(2) | 3.124(4) | 151(4) |
| | O3A–H3AB...O43 ^m | 0.815 (18) | 2.01(3) | 2.769(4) | 156(4) |
| | O1A–H1AA...O43 | 0.832 (19) | 2.13(3) | 2.733(9) | 129(3) |
| | O1B–H1BA...O43 | 0.82(2) | 2.01(7) | 2.764 (11) | 153(13) |

^a $1-x, 1/2+y, 1/2-z$. ^b $1+x, -1/2-y, 1/2+z$. ^c $1-x, -1/2+y, 1/2-z$. ^d $1-x, -y, 1-z$. ^e $x, 1+y, z$. ^f $-x, 1/2+y, 3/2-z$. ^g $1-x, 1-y, 2-z$. ^h $x, -1+y, z$. ⁱ $-x, -1/2+y, 3/2-z$. ^j $x, 3/2-y, -1/2+z$. ^k $1+x, 1+y, z$. ^l $1-x, 1-y, 1-z$. ^m $-1+x, y, z$.

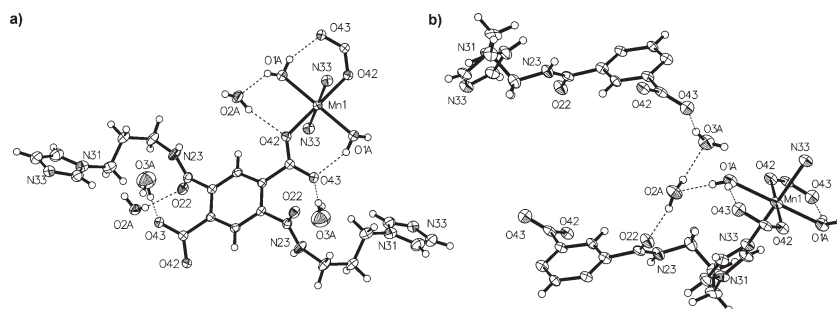


Fig. 4 Views showing the placement of water solvent molecules and resulting hydrogen bonding interactions within (a) **3** and (b) **4**. Displacement ellipsoids are drawn at the 50% probability level.

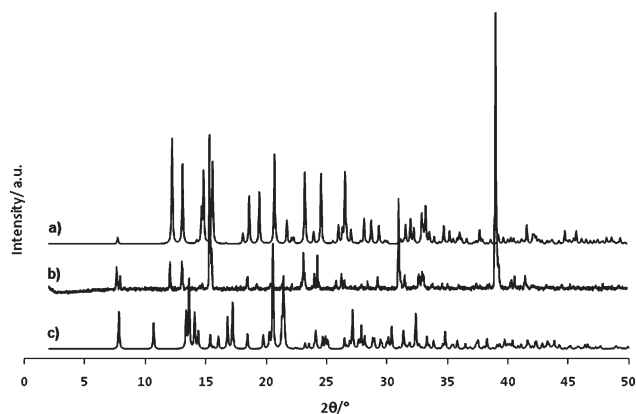


Fig. 5 (a) The PXRD pattern of **3** simulated from the single crystal data, (b) the experimental PXRD for **3** and (c) the PXRD pattern of **4** simulated from single crystal data.

materials but it is rare that the nature of such species can be determined.¹⁹ Our study illustrates the complexity involved in designing MOF structures where isomeric framework structures can readily form, complicating the targeting of materials with designed properties.

Experimental

Materials and general methods

All chemicals and solvents were purchased from Alfa-Aesar, Fisher Scientific or Sigma-Aldrich and were used as received without any further purification. All manipulations were performed under aerobic conditions. Solid-state infrared spectra were recorded in the 400–4000 cm^{-1} range using a Thermo Scientific iD5 diamond ATR on a Nicolet iS5 FT-IR Spectrometer. Elemental analyses were performed by Stephen Boyer, London Metropolitan University. NMR spectra were obtained using a Bruker Avance400 spectrometer. Powder X-ray diffraction experiments were performed on a PANalytical X'Pert Pro MPD in Bragg-Brentano geometry, with monochromated $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$).

Synthesis

2,5-Bis(3-(1-imidazolyl)propylcarbamoyl)terephthalic acid (biptaH₂). To a solution of 1-(3-aminopropyl)imidazole (3.9 mL, 32.7 mmol) in *N,N*-dimethylformamide (30 mL) was added 1,2,4,5-benzene-tetracarboxylic dianhydride (3.3 g, 15.1 mmol) and the resultant mixture was heated at 90 °C for 24 h. After cooling to room temperature the precipitate was filtered, washed with *N,N*-dimethylformamide and dried under high vacuum to yield 2,5-bis(3-(1-imidazolyl)propylcarbamoyl)terephthalic acid as a white solid (4.17 g, 59%). Single crystals suitable for X-ray diffraction were grown from dissolution of the product (20 mg) in the minimum amount of water and subsequent layering of tetrahydrofuran on top of this solution. ¹H-NMR (400 MHz; D₂O) δ ppm: 8.70 (2H, s), 7.55 (2H, s), 7.53–7.51 (2H, m), 7.42–7.40 (2H, m), 4.33 (4H, t, *J* 6.8), 3.34 (4H, t, *J* 6.5), 2.17 (4H, qnt, *J* 6.8). ¹³C-NMR (100 MHz, D₂O)

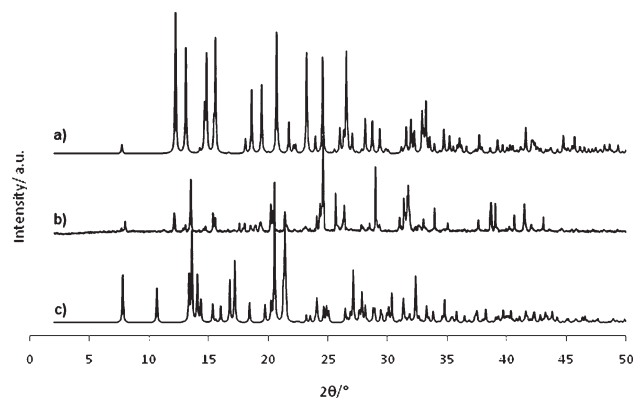


Fig. 6 (a) The PXRD pattern of **3** simulated from single crystal data, (b) the experimental PXRD for **4** and (c) the PXRD pattern of **4** simulated from single crystal data.

δ ppm = 174.18 (C=O), 171.86 (C=O), 138.39 (C–Ar), 136.03 (C–Ar), 135.13 (CH–Ar), 126.70 (CH–Ar), 121.61 (CH–Ar), 120.25 (CH–Ar), 46.25 (CH₂), 35.92 (CH₂), 28.99 (CH₂). FT-IR (ATR, cm^{-1}): 3222br, 3112w, 3049w, 1703.4m, 1639s, 1587m, 1543s, 1433w, 1407m, 1368w, 1341s, 1284m, 1268sm, 1241w, 1198w, 1141w, 1092m, 1039w, 1009w, 920w. Elemental analysis (%) calculated for C₂₂H₂₄N₆O₆: C, 56.40; H, 5.16; N, 17.94; found: C, 56.24; H, 5.07; N, 17.86.

[Zn(bipta)]_∞ (1). Single crystals of **1** suitable for X-ray diffraction were grown by slow diffusion of a solution of zinc(II) nitrate tetrahydrate (64 mg, 213.7 mmol) in acetonitrile (17 mL) into a solution of biptaH₂ (20 mg, 42.7 mmol) in water (3 mL) at ambient temperature over several days. Colourless plates were obtained in a 40% yield (9 mg, 16.9 mmol), based on ligand. FT-IR (ATR, cm^{-1}): 3253br, 3130w, 2954w, 1610s, 1563s, 1536m, 1490m, 1462m, 1438m, 1393m, 1337s, 1308m, 1278m, 1232m, 1137m, 1097s, 1030m, 957m. **1** gave inconsistent elemental analysis results due to variations in solvent content within the framework structure: see the main text for further discussion.

{[Co(bipta)(H₂O)₂].4H₂O]_∞ (2). In a similar procedure to the synthesis of **1**, single crystals of **2** were grown by slow diffusion of a solution of cobalt(II) nitrate hexahydrate (62 mg, 213.7 mmol) in methanol (17 mL) into a solution of biptaH₂ (20 mg, 42.7 mmol) in water (3 mL). Pink rods were obtained in a 30% yield (8 mg, 12.6 mmol), based on ligand. FT-IR (ATR, cm^{-1}): 3302br, 3136w, 1616s, 1552s, 1466w, 1438m, 1399s, 1360m, 1334m, 1297m, 1278m, 1232m, 1191w, 1110m, 1090s, 1032w, 944m. Elemental analysis (%) calculated for CoC₂₂H₃₄N₆O₁₂: C, 41.71; H, 5.41; N, 13.27; found: C, 41.75; H, 5.32; N, 13.17.

{[Mn(bipta)(H₂O)₂].4H₂O]_∞ (3). Single crystals of **3** were grown by slow diffusion of a solution of manganese(II) nitrate hexahydrate (61 mg, 213.7 mmol) in methanol (17 mL) into a solution of biptaH₂ (20 mg, 42.7 mmol) in water (3 mL). Colourless blocks were obtained in a 41% yield (11 mg, 17.5 mmol), based on ligand. FT-IR (ATR, cm^{-1}): 3306br, 3136w, 2934w, 1621m, 1556s, 1529m, 1438w, 1404s, 1372m, 1336s, 1307m, 1283m, 1242m, 1144w, 1107m, 1092s, 939m.

Table 3 Crystal data for biptaH₂ and complexes **1–5**

| | biptaH ₂ | 1 | 2 | 3 | 4 | 5 |
|--|--|---|--|--|--|--|
| Formula | C ₂₂ H ₃₄ N ₆ O ₁₁ | Zn ₂ (C ₂₂ H ₂₂ N ₆ O ₆) ₂ | CoC ₂₂ H ₃₄ N ₆ O ₁₂ | MnC ₂₂ H ₃₄ N ₆ O ₁₂ | MnC ₂₂ H ₃₄ N ₆ O ₁₂ | CuC ₂₂ H ₅₈ N ₆ O ₂₄ |
| <i>M_r</i> | 557.62 | 1063.65 | 633.48 | 629.49 | 629.49 | 854.28 |
| Crystal system | Monoclinic | Tetragonal | Monoclinic | Monoclinic | Triclinic | Triclinic |
| Space group | <i>P2₁/c</i> | <i>I4₁/amd</i> | <i>P2₁/c</i> | <i>P2₁/c</i> | <i>P1</i> | <i>P1</i> |
| <i>a</i> /Å | 11.45636(11) | 19.496(7) | 11.4211(3) | 11.4968(5) | 7.2247(16) | 9.3009(6) |
| <i>b</i> /Å | 8.63998(9) | 19.496(7) | 8.5517(2) | 8.5830(3) | 9.021(2) | 10.5787(7) |
| <i>c</i> /Å | 13.46297(15) | 15.769(7) | 13.4463(3) | 13.5611(5) | 11.662(2) | 11.2121(7) |
| α (°) | 90 | 90 | 90 | 90 | 97.094(17) | 92.593(5) |
| β (°) | 105.1417(11) | 90 | 93.083(2) | 93.193(2) | 98.186(17) | 97.681(5) |
| γ (°) | 90 | 90 | 90 | 90 | 110.63(2) | 111.597(6) |
| <i>V</i> /Å ³ | 1286.34(2) | 5994(4) | 1311.40(5) | 1336.09(9) | 691.6(3) | 1011.18(11) |
| <i>Z</i> | 2 | 2 | 2 | 2 | 1 | 1 |
| <i>T</i> /K | 90 | 90 | 90 | 90 | 90 | 90 |
| λ /Å | 1.5418 | 1.5418 | 1.5418 | 0.71073 | 0.71073 | 1.5418 |
| μ /mm ⁻¹ | 0.99 | 1.487 | 5.808 | 1.565 | 0.55 | 1.564 |
| ρ_{calc} g/cm ³ | 1.44 | 1.179 | 1.604 | 0.569 | 1.511 | 1.403 |
| Reflections collected | 10 819 | 11 142 | 14 467 | 12 461 | 6521 | 6106 |
| Independent reflections, [<i>R</i> _{int}] | 2315 [0.013] | 1616 [0.037] | 2656 [0.033] | 3057 [0.026] | 3410 [0.071] | 3903 [0.044] |
| <i>R</i> ₁ , <i>wR</i> ₂ | 0.0387, 0.104 | 0.0974, 0.294 | 0.038, 0.113 | 0.0496, 0.158 | 0.066, 0.177 | 0.0613, 0.156 |
| Goodness-of-fit, <i>S</i> | 1.063 | 1.17 | 1.09 | 1.10 | 1.03 | 1.09 |

Elemental analysis (%) calculated for MnC₂₂H₃₄N₆O₁₂: C, 41.98; H, 5.44; N, 13.35; found: C, 41.88; H, 5.35; N, 13.24.

{[Mn(bipta)(H₂O)₂] \cdot 4H₂O}_∞ (**4**). Single crystals of **4** were grown using the same method as for **3** except that the metal salt was dissolved in acetonitrile (3 mL). Colourless blocks were obtained in a 33% yield (9 mg, 14.3 mmol), based on ligand. FT-IR (ATR, cm⁻¹): 3305.5br, 3139w, 1622m, 1548s, 1463w, 1436m, 1402s, 1332m, 1294m, 1193m, 1142w, 1108m, 1088m, 938w.

{[Cu(bipta)(H₂O)₂] \cdot 16H₂O}_∞ (**5**). Single crystals of **5** were grown by slow diffusion of a solution of copper(II) nitrate hexahydrate (50 mg, 213.7 mmol) in water (17 mL) into a solution of biptaH₂ (20 mg, 42.7 mmol) in water (3 mL) at ambient temperature over several days. Blue plates were obtained in a 47% yield (13 mg, 19.9 mmol), based on ligand. FT-IR (ATR, cm⁻¹): 3293br, 3129w, 1629s, 1602s, 1536s, 1456w, 1405m, 1367m, 1337s, 1291m, 1240m, 1191w, 1146w, 1106s, 1031w, 956m.

X-Ray crystallography. Single-crystal X-ray diffraction experiments were performed on either a Bruker AXS SMART APEX CCD area detector diffractometer equipped with an Oxford Cryosystems open flow cryostat operating at 90 K using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å), or on an Oxford Diffraction SuperNova CCD area detector diffractometer operating at 90 K using mirror-monochromated Cu K α radiation ($\lambda = 1.5418$ Å). The structures were solved by direct methods using SHELXS97 and refined by full-matrix least squares on *F*² using SHELXL97.²⁰ [Zn(bipta)]_∞ **1** contained disordered solvent moieties, which could not be modelled and these were treated with PLATON SQUEEZE.²¹ In all crystal structures disorder was observed either in the bipta²⁻ ligands or in guest solvent molecules, details of how disorder was modelled and how water hydrogen atoms were treated are given in the supplementary cifs. Topological analyses were performed using TOPOS.²² The crystal data for biptaH₂ and **1–5** are listed in Table 3.

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