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Crystallographic investigation into the self-assembly, guest binding, and flexibility of urea functionalised metal-organic frameworks

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ABSTRACT

Introduction of hydrogen bond functionality into metal-organic frameworks can enhance guest binding and activation, but a combination of linker flexibility and interligand hydrogen bonding often results in the generation of unwanted structures where the functionality is masked. Herein, we describe the self-assembly of three materials, where Cd$^{2+}$, Ca$^{2+}$, and Zn$^{2+}$ are linked by $N,N'$-bis(4-carboxyphenyl)urea, and examine the effect of the urea units on structure formation, the generation of unusual secondary building units, structural flexibility, and guest binding. The flexibility of the Zn MOF is probed through single-crystal to single-crystal transformations upon exchange of DMF guests for CS$_2$, showing that the lability of the [Zn$_4$(RCOO)$_6$] cluster towards solvation enables the urea linkers to adopt distorted conformations as the MOF breathes, even facilitating rotation from the trans/trans to the trans/cis conformation without compromising the overall topology. The results have significant implications in the mechanistic understanding of the hydrolytic stability of MOFs, and in preparing heterogeneous organocatalysts.

ARTICLE HISTORY

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KEYWORDS

Metal-organic frameworks; urea; organocatalysis; hydrogen bonding

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Introduction

Metal-organic frameworks (MOFs) are network materials comprising metal ion or cluster secondary building units (SBUs) linked by organic linkers into multidimensional structures that often exhibit considerable porosity (1–3). Many examples contain arrays of chemically addressable pores, with functionalised derivatives acting as ‘crystalline molecular flasks’ (4, 5) and finding application in guest binding and activation for heterogeneous catalysis (6–10).
expected pillared primitive cubic topology, as a conse-
tquence of hydrogen bonding between the urea groups of
Zn metal cations, Cd[4,4ʹ-bipyridine in solvothermal syn-
thesis with DMF. The structures were solved using ShelxT
(37) and refined against F² using Shelx2015 (46) within Olex2 (47). [Cd(L)
DMF]n, was treated as a two component twin related by a
2-fold rotation about the 100 direction. The twin com-
ponent fractions refined to 0.421(6)/0.579(6) giving sig-
ificant improvement, however, probably due to some
unaccounted for twinning, only the Cd atom was refined
with anisotropic atomic displacement parameters (adps).

Figure 1. (Colour online) (a) H-bond donor groups incor-
porated into MOFs. (b) Structure-directing H-bonding be-
tween urea and carboxylate units of different nets in an
interpenetrated Zn MOF (redrawn from CCDC deposition 1011797). (c) Chemical structure of the ligand N,Nʹ-bis(4-carboxyphenyl)urea (LH₂) used in this
study. (d) Structures of the three different urea conforma-
tions.

For example, grafting hydrogen bond donor functional-
sity, such as amides (11–20), ureas (21–32), thioureas (33),
and squaramides (34–36), (Figure 1(a)) onto the organic scaffold
of the MOF can enhance properties including carbon
dioxide capture (13, 15, 17, 18), anion binding (20, 21), sensing
(28), and organocatalytic activity (6). Urea-functionalised
MOFs in particular have been found to catalyse Friedel-
Crafts reactions between pyrroles and nitroalkenes (22,
24, 27, 29, 31), Henry reactions between aldehydes and
nitromethane (23), and the methanolysis of epoxides (25).

Direct synthesis of urea-containing MOFs, by introd-
uction of urea moieties into organic linkers to target specific
topologies in an isoreticular synthetic approach, is com-
licated by the possibility of structure-directing hydro-
gen bonding between the linkers inducing unexpected
or unwanted MOF structures. For example, we have previ-
ously reported that the use of N,Nʹ-bis(4-pyridyl)urea
instead of 4,4ʹ-bipyridine in solvothermal syntheses with
Zn²⁺ sources and dicarboxylic acids results in MOFs with
interpenetrated diamondoid topology, rather than the
expected pillared primitive cubic topology, as a conse-
tquence of hydrogen bonding between the urea groups of
the pillar and the carboxylate groups of the ligand direct-
ing structure formation (Figure 1(b)) (37). The formation of
hydrogen bonds between different parts of the MOF
structure could mask potential catalytic sites, and so an
understanding of how it can be avoided when using lig-
ands such as N,Nʹ-bis(4-carboxyphenyl)urea (LH₂, Figure
1(c)) is essential. Additionally, hydrogen bonding moieties
often introduce structural flexibility; urea units have rota-
tional freedom around the C–N–C moieties and can adopt
(Figure 1(d)) three different conformations – trans/trans,
trans/cis, cis/cis – with the trans/trans conformation (also
known as the syn, syn conformation) expected to be opti-
mal for organocatalysis and guest binding (38, 39). Herein,
we describe the direct self-assembly and solid-state struc-
tures of three coordination polymers of LH₂ and different
metal cations, Cd²⁺, Ca²⁺ and Zn²⁺, discussing the effect of
urea incorporation on structure, formation of novel
inorganic SBUs, guest binding, and flexibility. We probe
the guest binding properties of the Zn MOF with CS₂ as a
mimic for CO₂ and show that incorporation of the guest
induces single-crystal to single-crystal (SCSC) trans-
fomations with notable changes in both linker confor-
mation and SBU coordination chemistry. These results have sig-
ificant implications in the understanding of activation, guest
binding and hydrolysis of H-bond functionalised MOFs.

Experimental

General

All chemicals and solvents were purchased from Alfa
Aesar, Fisher Scientific, VWR, and Sigma Aldrich, and used
as received.

Crystallography

Single Crystal X-ray diffraction data for [Cd(L)(DMF)]ₙ
and [Ca₂(L)₃(DMF)₃(H₂O)]ₙ, were collected using a Rigaku
AFC12 goniometer equipped with an enhanced sensitivity
(HG) Saturn724+ detector mounted at the window of an
FR-E+ SuperBright molybdenum rotating anode generator
with VHF Varimax optics (70 μm focus) equipped with an
Oxford Cryosystems cryostream device (EPSRC UK National
Crystallography Service) (40). Data were collected using
CrystalClear-SM Expert 3.1 b27 (41) and processed with
CrysAlisPro 1.171.38.43 (42). Single crystal data for both solv-
ates of [Zn₉O(L)₉(DMF)]ₙ as well as their daughter prod-
ucts isolated during soaking in CS₂ were collected using a
Bruker D8 Venture goniometer with a Bruker PHOTON II
detector and dual ImuS 3.0 microfocus sources (Cu and Mo Kα)
equipped with an Oxford Cryosystems n-Helix device.
Mo Kα radiation was used for all data collections except
[Zn₉O(L)₉(DMF)(H₂O)]ₙ, where Cu Kα was used (University
of Glasgow). Data were collected using APEX3 Ver. 2016.9-0
(43) and processed with SAINT V8.37A (44).

The structures were solved using ShelX (45) and refined
against F² using Shelx2015 (46) within Olex2 (47). [Cd(L)
DMF]ₙ, was treated as a two component twin related by a
2-fold rotation about the 100 direction. The twin com-
ponent fractions refined to 0.421(6)/0.579(6) giving sig-
ificant improvement, however, probably due to some
unaccounted for twinning, only the Cd atom was refined
with anisotropic atomic displacement parameters (adps).
For this structure SQUEEZE (48) was only used to calculate the solvent accessible volume (32 Å³) however for all other structures reported herein SQUEEZE was used to calculate and account for the electron density within the solvent accessible void; details are given in Table 1. Disorder was present and modelled as two 0.5 occupied sites in one linker for both [Ca\textsubscript{L}(DMF)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}]\textsubscript{n} and [Zn\textsubscript{L}(DMF)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}]\textsubscript{n}. Distance restraints were used in the case of the disordered fragments and for the solvent (DMF and CS\textsubscript{2}) geometry. For the samples treated with CS\textsubscript{2} all the structures showed residual electron density on the Zn sites possibly due to unaccounted for twinning however treatment as a two component crystal was not satisfactory and was not used.

**Synthesis**

LH\textsubscript{2} was synthesised by a modified literature procedure (49).

[Cd(L)(DMF)]\textsubscript{3}n. Cadmium nitrate tetrahydrate (0.010 g, 0.032 mmol), LH\textsubscript{2} (0.009 g, 0.030 mmol) and N,N-dimethylformamide (DMF, 5 ml) were added to a 25 ml Pyrex reagent bottle and sonicated. The resulting solution was placed in the oven at 100 °C for 48 h. The bottle was removed from the oven after this period and allowed to cool to room temperature. The crystals were left to stand in their mother solution.

Crystal data for [Cd(L)(DMF)]\textsubscript{3}n. C\textsubscript{24}H\textsubscript{31}CdN\textsubscript{2}O\textsubscript{8}, M\textsubscript{r} = 629.94, crystal dimensions 0.07 × 0.05 × 0.01 mm, Monoclinic, a = 9.1728 (7) Å, b = 15.2062 (14) Å, c = 19.768 (2) Å, V = 2749.5 (5) Å\textsuperscript{3}, T = 100 K, space group P2\textsubscript{1}/c (no. 14), Z = 4, 18,150 measured reflections, 4,767 unique (R\textsubscript{int} = 0.147). Data were not merged as from a two component twin and all 18,510 reflections were used in all calculations. The final R\textsubscript{1} = 0.161 for 11,215 (of 18510) observed data [R(F\textsuperscript{2} > 2σ(F\textsuperscript{2})] and wR(F\textsuperscript{2}) = 0.389 (all data). Crystal structure data are available from the CCDC, deposition number 1558143.

[Zn\textsubscript{L}(DMF)]\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}n, Calcium nitrate tetrahydrate (0.008 g, 0.033 mmol), LH\textsubscript{2} (0.010 g, 0.033 mmol) and DMF (10 ml) were added to a 50 ml Pyrex reagent bottle and sonicated. The resulting solution was placed in the oven at 100 °C for 48 h. The bottle was removed from the oven after this period and allowed to cool to room temperature. The crystals were left to stand in their mother solution.

Crystal data for [Ca\textsubscript{L}(DMF)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}]\textsubscript{n}. C\textsubscript{84}H\textsubscript{88}Ca\textsubscript{5}N\textsubscript{13}O\textsubscript{30}-6.75(C\textsubscript{5}H\textsubscript{2}NO)-3.5(H\textsubscript{2}O), M\textsubscript{r} = 2503.42, crystal dimensions 0.22 × 0.06 × 0.04 mm, Triclinic, a = 16.0056 (4) Å, b = 18.4778 (6) Å, c = 31.0206 (4) Å, V = 8431.9 (4) Å\textsuperscript{3}, T = 100 K, space group P-1 (no. 2), Z = 2, 91,045 measured reflections, 29,730 unique (R\textsubscript{int} = 0.083) which were used in all calculations. The final R\textsubscript{1} = 0.109 for 19,792 observed data [R(F\textsuperscript{2} > 2σ(F\textsuperscript{2})] and wR(F\textsuperscript{2}) = 0.347 (all data).

Approximately 30% of the cell volume is not occupied by the framework and contains diffuse and disordered solvent molecules. This electron density was accounted for using SQUEEZE within PLATON (48) which calculated a solvent accessible volume of 2565 Å\textsuperscript{3} containing 681 electrons (the equivalent of ~17 molecules of DMF) per unit cell. Crystal structure data are available from the CCDC, deposition number 1558144.

[Zn\textsubscript{L}(DMF)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}]n-I. Zinc nitrate hexahydrate (0.050 g, 0.168 mmol), LH\textsubscript{2} (0.050 g, 0.167 mmol) and DMF (20 ml) were added to a 100 ml reagent bottle and sonicated. The resulting solution was placed in the oven at 90 °C for 24 h. The bottle was removed from the oven after this period and allowed to cool to room temperature. The crystals were left to stand in their mother solution. Crystals of [Zn\textsubscript{L}(DMF)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}]n-II were also isolated from this synthesis in the same container. As the two solvates are identical in connectivity and topology they were not separated, and referred to as [Zn\textsubscript{L}(DMF)\textsubscript{3}]n.

Crystal data for [Zn\textsubscript{L}(DMF)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}]n-I. C\textsubscript{51}H\textsubscript{44}N\textsubscript{17}Zn\textsubscript{6}(C\textsubscript{5}H\textsubscript{2}NO), M\textsubscript{r} = 1756.99, crystal dimensions 0.16 × 0.12 × 0.07 mm, Monoclinic, a = 16.0084 (5) Å, b = 30.1963 (14) Å, c = 20.4622 (8) Å, V = 9778.3 (7) Å\textsuperscript{3}, T = 100 K, space group P2\textsubscript{1}/c (no. 14), Z = 4, 55,552 measured reflections, 24,084 unique (R\textsubscript{int} = 0.052) which were used in all calculations. The final R\textsubscript{1} = 0.087 for 18,205 observed data [R(F\textsuperscript{2} > 2σ(F\textsuperscript{2})] and wR(F\textsuperscript{2}) = 0.243 (all data). Approximately 10% of the cell volume is not occupied by the framework and contains diffuse and disordered solvent molecules. This electron density was accounted for using SQUEEZE within PLATON (48) which calculated a solvent accessible volume of 956 Å\textsuperscript{3} containing 154 electrons (the equivalent of ~3.85 molecules of DMF) per unit cell. Crystal structure data are available from the CCDC, deposition number 1558145.

Crystal data for [Zn\textsubscript{L}(DMF)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}]n-II. C\textsubscript{51}H\textsubscript{44}N\textsubscript{17}Zn\textsubscript{6}(C\textsubscript{5}H\textsubscript{2}NO), M\textsubscript{r} = 1537.71, crystal dimensions 0.26 × 0.24 × 0.17 mm, Monoclinic, a = 15.7982 (10) Å, b = 30.2971 (17) Å, c = 20.4468 (14) Å, V = 9644.8 (11) Å\textsuperscript{3}, T = 100 K, space group P2\textsubscript{1}/c (no. 14), Z = 4, 123,520 measured reflections, 23,849 unique (R\textsubscript{int} = 0.102) which were used in all calculations. The final R\textsubscript{1} = 0.068 for 13,455 observed data [R(F\textsuperscript{2} > 2σ(F\textsuperscript{2})] and wR(F\textsuperscript{2}) = 0.236 (all data). Approximately 33% of the cell volume is not occupied by the framework and contains diffuse and disordered solvent molecules. This electron density was accounted for using SQUEEZE within PLATON (48) which calculated a solvent accessible volume of 3164 Å\textsuperscript{3} containing 905 electrons (the equivalent of ~22.6 molecules of DMF) per unit cell. Crystal structure data are available from the CCDC, deposition number 1558146.

A small amount of [Zn\textsubscript{L}(DMF)\textsubscript{3}]n was removed from its mother solution by pipette (ca. 2 ml) and added to a
Table 1. Crystallographic data comparison.

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<tr>
<th>Crystallographic Data for [Zn(\text{O-(L)}_2\text{(DMF)(H\rightleftharpoons\text{O)}_2}\rightleftharpoons\text{DMF})_n] (no. 14),</th>
<th>Crystallographic Data for [Zn(\text{O-(L)}_2\text{(DMF)(H\rightleftharpoons\text{O)}_2}\rightleftharpoons\text{DMF})_n] (no. 14),</th>
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<td>Zn(<em>4\rightleftharpoons\text{O-(L)}\rightleftharpoons\text{C}</em>{46}H_{30}N_2O_{16}\rightleftharpoons\text{Zn}_{2}\text{3(\text{C}_2H_4\text{NO})-9(\text{CS}_2)}\rightleftharpoons\text{M} = 2076.69, crystal dimensions</td>
<td>Zn(<em>4\rightleftharpoons\text{O-(L)}\rightleftharpoons\text{C}</em>{46}H_{30}N_2O_{16}\rightleftharpoons\text{Zn}_{2}\text{3(\text{C}_2H_4\text{NO})-9(\text{CS}_2)}\rightleftharpoons\text{M} = 2076.69, crystal dimensions</td>
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All crystallographic data are summarised and compared in Table 1. CCDC 1558143–1558149 contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre; see https://www.ccdc.cam.ac.uk/.

**Results and discussion**

The urea-dicarboxylate ligand, $\text{LH}_2$, was prepared on the gram scale according to a modification of a literature procedure in two steps from $t$-butyl 4-aminobenzoate and carbonyldiimidazole (49). Attempts were subsequently made to prepare MOFs containing the ligand with free urea units to examine guest binding. Solvothermal synthesis with $\text{Cd(NO}_3)_2\cdot4\text{H}_2\text{O}$ in DMF at 100 °C for 48 h resulted in the isolation of the one-dimensional coordination polymer $[\text{Cd(L)(DMF)}]_n$. The material consists of chains of $\text{L}^2$ molecules connected by seven-coordinate $\text{Cd}^{2+}$ cations with distorted pentagonal bipyramidal geometry (Figure 2(a)). The $\text{Cd}^{2+}$ centres coordinate to both oxygen atoms of the carboxylate units of two molecules of $\text{L}^2$, linking them in a trans manner, with three DMF molecules occupying the remainder of the coordination sphere. The 1D chains that result have the urea N-H units projecting only in one direction for any given chain, and these form bifurcated H-bond interactions (Figure 2(b)) with the carboxylate units of the two $\text{L}^2$ molecules around the $\text{Cd}^{2+}$ SBUs of adjacent chains (N1--O5 = 2.784, N1--O3 = 3.232 Å; N2--O3 = 2.785, N2--O5 = 3.431 Å). The linear packing arrangement of the chains results in 2D H-bonded grids, with all urea units involved in hydrogen bonding (Figure 2(c)). The grids then stack upon each other with no significant intermolecular interactions.

The seven coordinate SBU has only been observed in one other $\text{Cd}^{2+}$ coordination polymer – a related material with tetrabromoterephthalate linkers (50) – but derivatives where the DMF ligands are replaced by water to form coordination polymers are also known (51, 52). The urea units of $\text{L}^2$ clearly direct the formation of this structure, and would be unavailable for guest binding.

When $\text{LH}_2$ is combined with $\text{Ca(NO}_3)_2\cdot4\text{H}_2\text{O}$ in DMF and heated to 100 °C for 48 h, a very small quantity of crystals of $[\text{Ca}_5(\text{L})_3(\text{DMF})_3(\text{H}_2\text{O})_2]_n$ results. The structure contains infinite chains of calcium cations linked by carboxylate units of $\text{L}^2$. There are five crystallographically independent $\text{Ca}^{2+}$ cations in the chains, but each has the same overall seven-coordinate, distorted pentagonal bipyramidal geometry (Figure 3(a)).

![Figure 2](image-url)  
**Figure 2.** (Colour online) The solid state structure of $[\text{Cd(L)(DMF)}]_n$. (a) One dimensional chains of $\text{Cd}^{2+}$ cations linked by molecules of $\text{L}^2$. (b) Interligand hydrogen bonding between the urea units of molecules of $\text{L}^2$ from one chain and carboxylate units of molecules of $\text{L}^2$ from an adjacent chain. (c) Assembly of the one dimensional polymers of $[\text{Cd(L)(DMF)}]_n$ into an infinite two dimensional grid structure, with chains of individual sheets coloured red and blue. H atoms other than the N-H units removed for clarity in part (b).

![Figure 3](image-url)  
**Figure 3.** (Colour online) (a) Schematic of the coordination sphere of the $\text{Ca}^{2+}$ ions in $[\text{Ca}_5(\text{L})_3(\text{DMF})_3(\text{H}_2\text{O})_2]_n$. (b) The coordination environments of the five crystallographically independent $\text{Ca}^{2+}$ ions in the crystal structure of $[\text{Ca}_5(\text{L})_3(\text{DMF})_3(\text{H}_2\text{O})_2]_n$. (c) Extended structure of $[\text{Ca}_5(\text{L})_3(\text{DMF})_3(\text{H}_2\text{O})_2]_n$ viewed down the crystallographic $a$ axis, showing triangular channels. (d) Bifurcated hydrogen bonding of a DMF molecule by the urea unit of one of the linkers, also showing the two coordination motifs to the $\text{Ca}^{2+}$ cations in the structure. (e) Alternative view down the crystallographic $b$ axis, showing further small pores. Disorder, non-coordinated solvents and hydrogen atoms removed for clarity.
One carboxylate unit of \( \text{L}^2 \) chelates with both its oxygen atoms to the \( \text{Ca}^{2+} \) cation, with each oxygen coordinating to an adjacent calcium centre to overall bridge three \( \text{Ca}^{2+} \) cations in a \((\eta^2:\eta^2:\mu)\) fashion. Two further carboxylate units of \( \text{L}^2 \) molecules bridge from the \( \text{Ca}^{2+} \) cation to adjacent \( \text{Ca}^{2+} \) centres above and below, both in a \((\eta^2:\eta^2:\mu)\) motif. Each \( \text{Ca}^{2+} \) therefore coordinates to six carboxylate oxygen atoms from five different ligands, with a final DMF or water molecule making up the coordination sphere (Figure 3(b)). Each molecule of \( \text{L}^2 \) links the infinite 1D chains of \( \text{Ca}^{2+} \) ions through a \((\eta^2:\eta^2:\mu)\) motif at one carboxylate and a \((\eta^2:\eta^2:\mu)\) motif at the other. The chains run down the crystallographic \( a \) axis, and are linked into an approximately hexagonal array by molecules of \( \text{L}^2 \).

There are five crystallographically independent linker molecules, all of which experience some distortion from an idealised planar structure. Small triangular pores run down the crystallographic \( a \) axis (Figure 3(c)) and these spaces are filled in the crystal structure with a large number of water and DMF solvent molecules, with two of the five independent urea units binding water guests through a bifurcated H-bonding motif (N1C--O5W = 3.381, N2C--O5W = 2.940 Å; N1D--O4W = 2.827, N2D--O4W = 3.005 Å) and a further two urea units binding DMF molecules (N1--O61S = 2.832, N2--O61S = 2.810 Å; N1A--O56S = 3.377, N2A--O56S = 2.809 Å) in a similar manner (Figure 3(d)). There are also small voids between the chains perpendicular to the channels (Figure 3(e)). The 1D chains of \( \text{Ca}^{2+} \) cations units in \([\text{Ca}_2\text{L}_3\text{DMF}_3\text{H}_2\text{O}]_n\) enforce a topology in which the urea moieties are not involved in any inter-ligand hydrogen bonding. Unfortunately we were unable to find suitable synthetic conditions to access any more than a few crystals per reaction, and so alternative MOFs were sought for study.

Solvothermal reaction of \( \text{LH}_2 \) with \( \text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O} \) in DMF for 24 h at 90 °C yielded block-shaped crystals of \([\text{Zn}_3\text{O}_5\text{L}_3\text{DMF}_3\text{H}_2\text{O}]_2 \cdot \text{H}_2\text{O}\)\(-II\), which is the well-known IRMOF topology first reported by Yaghi in 1999 for MOF-5 (also known as IRMOF-1), \([\text{Zn}_n\text{O}(_{\text{bd}}\text{c})_3]_n\) where \( _{\text{bd}} \) = 1,4-benzenedicarboxylate (53). The material has a slightly different SBU than the parent IRMOF structure; instead of four tetrahedral \( \text{Zn}^{2+} \) cations linked by a \( \mu_3^+ \text{O}^{2-} \) and six carboxylates, there are three tetrahedral \( \text{Zn}^{2+} \) centres and one octahedral \( \text{Zn}^{2+} \) cation with two additional coordinated DMF ligands (Figure 4(a)). This solvated SBU is rarely seen in IRMOF structures, but is known to occur when IRMOFs are prepared from linkers that are flexible (54, 55) or deviate from ideal linear geometry (56, 57). Whilst the \( \text{L}^2 \) linkers lie along linear edge connections positioning \( \text{Zn}^{2+} \) SBUs in the primitive cubic topology, the carboxyphenyl groups are disposed at approximately 145° rather than 180°, and the linkers also bow in and out of the plane, indicating significant flexibility (58). Indeed, \([\text{Zn}_3\text{O}_5\text{L}_3\text{DMF}_3]_2 \cdot \text{H}_2\text{O}\) is structurally similar to NJU-Bai2, a \( \text{Zn}^{2+} \) IRMOF prepared from an analogous ligand with a central amido group rather than a urea moiety (59). \([\text{Zn}_4\text{O}_6\text{L}_3\text{DMF}_3]_2 \cdot \text{H}_2\text{O}\) is triply interpenetrated, with three identical nets nested within one another (Figure 4(b)), but surprisingly there are no net hydrogen bonding interactions between the urea and carboxylate functionalities. Instead, in the crystal structure each of the three crystallographically independent urea units binds a DMF molecule through bifurcated hydrogen bonding to the formamide oxygens (N1--O40T = 2.696, N2--O40T = 2.942 Å; N1A--O11S = 2.848, N2A--O11S = 2.863 Å; N1B--O21S = 2.967, N2B--O21S = 2.850 Å).

Interestingly, a second set of crystals was observed after the solvothermal synthesis with different morphology – agglomerates of plates (Figure 4(c)) – which single crystal X-ray diffraction revealed to be a closely related material, \([\text{Zn}_n\text{O}(_{\text{bd}}\text{c})\text{DMF}_3]_2 \cdot \text{H}_2\text{O}\)\(-II\), with identical connectivity and topology to \([\text{Zn}_3\text{O}_5\text{L}_3\text{DMF}_3]_2 \cdot \text{H}_2\text{O}\)\(-I\) but a slightly different unit cell, presumably due to differing levels of solvation. Isolation of this additional phase is likely a consequence of the
flexibility of the MOF allowing for crystallisation of closely related solvates from one synthesis. As the topology and structure of the two are identical, and because mechanical manipulation would be the only possible method of separation, we refer to the combined material as simply [Zn₄O(L)₃(DMF)]ₙ in the remainder of the study.

We first reported the isolation of this material in our previous study of urea incorporation into MOFs (37) but did not fully describe the structure. During the preparation of this manuscript, a report detailing the synthesis of [Zn₄O(L)₃(DMF)]ₙ and its catalytic activity in the Friedel-Crafts reaction between indole and β-nitrostyrene was published (29). The fact that the urea groups are not involved in ‘host-host’ hydrogen bonding facilitates this reported catalytic activity once the bound DMF molecules are removed, further highlighting the importance of limiting these interactions by topological control during the design of organocatalytic MOFs.

As part of our attempts to understand the availability of the urea groups for guest binding within the pores of this MOF, we attempted to replace the DMF solvents of crystallisation with Cs₂ by soaking crystals of the MOF in this liquid CO₂ mimic. This approach has been successfully used to examine guest binding in coordination cages (60), but reported structures of MOFs with bound Cs₂ remain relatively rare (61–67). As with the recently published study (29), [Zn₄O(L)₃(DMF)]ₙ was found to be relatively unstable to solvent removal, but Cs₂ is a volatile nonpolar solvent that may allow for efficient activation, and samples maintained crystallinity on solvent exchange from DMF to Cs₂. Single crystal X-ray diffraction analysis on a sample that had been soaked in Cs₂ at room temperature for 4 days revealed that rather than exchanging bound DMF guests for Cs₂, one of the DMF ligands coordinated to the octahedral Zn²⁺ cation in [Zn₄O(L)₃(DMF)]ₙ (Figure 5(a)) was replaced with water in a SCSC transformation to form [Zn₄O(L)₃(DMF)(H₂O)]ₙ (Figure 5(b)). It has been shown previously that DMF can dynamically bind to the metal cluster in the archetypal material MOF-5 (68), and these results clearly demonstrate that, even in MOFs where the DMF interacts with the SBU sufficiently to be located crystallographically, it can still be exchanged under mild conditions for alternative ligands. This partially hydrated cluster could also be considered as an intermediate species in the hydrolysis of the MOF, and indeed a model for all Zn MOFs that contain the basic zinc acetate SBU, which are known to be particularly susceptible to hydrolysis (69). Whilst the topology of the MOF remains unchanged, the flexibility is apparent when comparing [Zn₄O(L)₃(DMF)(H₂O)]ₙ to the parent structure. The ability of the ligand to distort, combined with the labile coordination chemistry of the SBU, allows the MOF to deviate from an approximately cubic arrangement (Figure 5(a)) to a flatter structure reminiscent of a rhombohedron (Figure 5(b)).

Leaving the same batch of crystals in Cs₂ for a further 15 days, with daily replenishment of the Cs₂, resulted in a further SCSC transformation to [Zn₄O(L)₃]ₙ, where all coordinated solvents had been removed and the SBU has the conventional Zn₄O(RCO₂)₆ composition (Figure 5(c)). Additionally, guest exchange occurred, with significant quantities of Cs₂ now located and ordered within the pores of the MOF, replacing weakly-bound DMF molecules. Tellingly, the only DMF that remains within the pores is hydrogen bonded to the urea units (N₁–O₆D = 2.893, N₂–O₆D = 2.903 Å; N₁A–O₁D = 2.860, N₂A–O₁D = 2.843 Å; N₁B–O₁ID = 2.863, N₂B–O₁1D = 2.847 Å), indicating the strength of the interaction, with the Cs₂, located in the pores. While Cs₂ may be a good geometric mimic of CO₂, it is a weaker hydrogen bond acceptor, likely due to it having an opposite quadrupole moment and thus not being

Figure 5. (Colour online) Comparison of the solid-state structures of the Zn MOFs of L²⁻, showing the topology and the SBU. (a) The parent MOF, [Zn₄O(L)₃(DMF)]ₙ, from which (b) [Zn₄O(L)₃(DMF)(H₂O)]ₙ, (c) [Zn₄O(L)₃]ₙ, and (d) [Zn₄O(L)₃(DMF)]ₙ, were prepared by single-crystal to single-crystal transformations. Non-coordinated solvent, H atoms and disorder removed for clarity.
Table 2. Angles measured between central µ₄-O²⁻ ligands of the Zn₄ O SBUs in the Zn MOFs of L²⁻. All angles would be 90° in an ideal cubic structure; the largest standard deviation indicates the largest distortion.

<table>
<thead>
<tr>
<th>MOF</th>
<th>Angles/°</th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn₄ O(L)₃(DMF)₃]₄⁺</td>
<td>76.1, 76.1, 78.4, 81.5, 82.7, 85.9</td>
<td>10.5</td>
</tr>
<tr>
<td>[Zn₄ O(L)₃(DMF)₃]₂⁺</td>
<td>94.1, 97.3, 98.5, 100.4, 101.3, 103.0</td>
<td>11.6</td>
</tr>
<tr>
<td>[Zn₄ O(L)₃(DMF)(H₂O)]₄⁺</td>
<td>74.8, 74.8, 77.9, 79.7, 82.0, 83.8</td>
<td>11.6</td>
</tr>
<tr>
<td>[Zn₄ O(L)₃(DMF)(H₂O)]₂⁺</td>
<td>96.2, 98.0, 100.3, 101.2, 102.1, 103.4</td>
<td>17.8</td>
</tr>
<tr>
<td>[Zn₄ O(L)₃(DMF)₃]₂⁺</td>
<td>59.2, 68.2, 77.9, 81.0, 81.0, 86.7</td>
<td>13.0</td>
</tr>
<tr>
<td>[Zn₄ O(L)₃]₄⁺</td>
<td>69.8, 74.0, 77.7, 81.7, 83.9, 86.0</td>
<td>13.0</td>
</tr>
<tr>
<td>[Zn₄ O(L)₃(DMF)]₄⁺</td>
<td>76.6, 81.5, 82.4, 82.4, 87.7, 88.1</td>
<td>8.7</td>
</tr>
</tbody>
</table>

electronically analogous (60), and it is certainly a weaker hydrogen bond acceptor than DMF.

The structure still has a rhombohedral-like arrangement, but seems visually less distorted than [Zn₄ O(L)₃(DMF)(H₂O)]₄⁺. To attempt to quantify the flexibility-induced distortion, the angles between adjacent SBUs were measured for each MOF, taking the bridging µ₄-O²⁻ units of the Zn₄ O SBUs as their centres, and collated in Table 2. For a perfect cubic structure, twelve angles of 90° would be expected, but the non-linear geometry of L²⁻, coupled with its ability to bow out of the plane, means a range of angles are observed experimentally. The standard deviation was calculated as a metric to describe the magnitude of distortion, with larger standard deviations indicating more significant distortion from the idealised cubic arrangement. The two solvates of [Zn₄ O(L)₃(DMF)₃]₄⁺ have similar values, while [Zn₄ O(L)₃(DMF)(H₂O)]₄⁺ has the largest standard deviation, with angles ranging from ~60° to 120°, which is obvious from inspection of the structure (Figure 5(b)). [Zn₄ O(L)₃]₄⁺ lies between the two extremes.

On leaving the batch of crystals for 6 more days in CS₂, a more dramatic structural rearrangement occurs, again in a SCSC manner, to form [Zn₄ O(L)₃(DMF)]₄⁺ (Figure 5(d)). One of the three crystallographically independent urea ligands undergoes rotation from the trans/trans conformation to the trans/cis arrangement, dramatically changing both the length and geometry of the linker (as well as its ability to bind guests or act as an organocatalyst) without altering the connectivity or interpenetration of the MOF (70). To accommodate the distortion, the SBU picks up a DMF molecule, leaving one of the Zn⁺⁺ centres in a 5-coordinate trigonal bipyramidal geometry (Figure 5(d)), very rarely seen in MOFs with the zinc acetate SBU, while the rest remain tetrahedral. This coordinated DMF molecule is likely one of those previously bound at the urea groups – only one of the three urea moieties now H-bonds a DMF guest – but exchange with the outer solvent cannot be excluded as a possibility. CS₂ molecules fill the pores (Figure 6(a)).

The structure maintains a relatively cubic arrangement of the Zn₄ O SBUs (Figure 5(d)), despite the obvious deviation that occurs on rotation of the molecules of L²⁻ from the trans/trans conformation (Figure 6(b)) to the trans/cis conformation (Figure 6(c)). In fact, the angles around the SBUs show even less deviation from an ideal cube than the parent material (Table 2), as the trans/cis linkers can still bridge two SBUs in an almost linear manner, despite their bent nature disposing the carboxylate units at an angle of approximately 120°, presumably generating the unusual mono-solvated Zn₄ O cluster.

The trans/cis linkers are, however, significantly shorter than the trans/trans linkers: the SBU-SBU distances measured between central µ₄-O²⁻ ligands is 17.55 Å for the trans/cis linker, as opposed to 19.68 Å and 19.94 Å for the two crystallographically independent trans/trans linkers, distances which are similar to those in the other Zn MOFs. The structure therefore is deviating from the cubic arrangement by pulling in two vertices on one side of the cube. We believe that the aforementioned flexibility of the material, derived from the L²⁻ ligands, allows it to endure such a significant change in linker length and geometry without breaking connectivity or altering interpenetration. This flexibility, combined with the labile coordination chemistry of the [Zn₄ O(RCO₂)₃] SBU, may, however, be responsible for the eventual framework collapse on drying – we were unable to successfully activate the porosity [Zn₄ O(L)₃(DMF)]₄⁺ to ascertain if the urea units enhanced CO₂ uptake.

Conclusions

We have exploited the flexibility of the urea-based linker, N,Nʹ-bis(4-carboxyphenyl)urea, to prepare three new framework materials with unusual SBUs: [Cd₄ L₃(DMF)]₄⁺, a one-dimensional coordination polymer; [Ca₄ (L)₃(DMF)₃(H₂O)]₄⁺ a three-dimensional MOF linked by infinite calcium chains;
and two solvates of $[\text{Zn}_4 \text{O}(\text{L})_4(\text{DMF})_2]_n$, which has the prototypical IRMOF topology. In concordance with previous work, the urea moieties in $[\text{Cd}(\text{L})(\text{DMF})]_n$ direct structure formation through interligand H-bonding, but the topological restrictions placed on the urea units in the other two materials leave them free to bind guest solvent molecules, and an independent report published during our study described $[\text{Zn}_4 \text{O}(\text{L})_4(\text{DMF})_2]_n$ to be an active organocatalyst as a result.

$\text{CS}_2$ was used as a mimic to probe guest binding in $[\text{Zn}_4 \text{O}(\text{L})_4(\text{DMF})_2]_n$, resulting in a number of single-crystal to single-crystal transformations that illustrated (i) the lability of the $[\text{Zn}_4 \text{O}(\text{RCO}_2)_4]_n$ SBU, capturing crystallographic snapshots in unusual states of solvation, and (ii) the flexibility of the framework, enabled by the facile coordination chemistry of the cluster and the flexibility of the organic ligand. Three additional crystal structures showed the MOF breathing as it exchanged DMF pore solvent for $\text{CS}_2$ eventually resulting in a dramatic conformational rearrangement of some of the urea units from the trans/trans to the trans/cis conformation, which are not capable of binding guests for organocatalysis. These results provide valuable structural insights into the dynamic behaviour of MOFs with flexible linkers upon activation, which have significant implications for the development of heterogeneous organocatalysts, and also give evidence for potential hydrolysis mechanisms. Additionally, we anticipate that $\text{CS}_2$ may be considered a mild alternative solvent for activating MOFs in future; whilst $[\text{Zn}_4 \text{O}(\text{L})_4(\text{DMF})_2]_n$ did collapse on solvent removal, $\text{CS}_2$ was the only solvent which penetrated its pores without damaging single crystals.

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References

(1) Furukawa, H.; Cordova, K.E.; O’Keeffe, M.; Yaghi, O.M. Science 2013, 341, 1230444.