The solvent-templating effect as the driving factor that influences the formation of crystalline materials based on the stacking of metallocycles†

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Received (in Durham, UK) 18th December 2006, Accepted 1st February 2007
First published as an Advance Article on the web 7th March 2007
DOI: 10.1039/b618495m

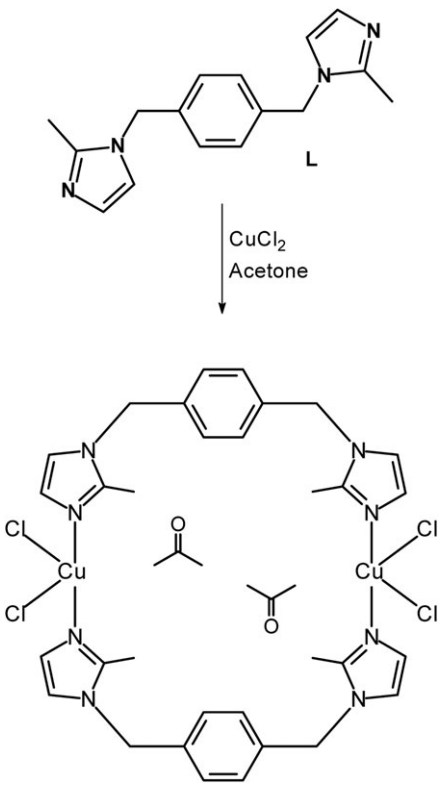
A series of recrystallisations of a 1 : 1 $CuCl_2$: **L** (**L** = 1,4-bis[(2-methylimidazol-1-yl)methyl]benzene) mixture from a variety of common solvents has been undertaken in order to investigate the effect of solvent templation on the resulting crystal forms. Single crystal X-ray diffraction analysis of eight new solvates of $[CuCl_2\mathbf{L}]_n$ reveals the solvent dependent formation of either a discrete dinuclear metallocycle or a one-dimensional coordination polymer. Conformational flexibility of both the ligand and the metal–ligand bonds results in the ability of these compounds to form a variety of structures.

Introduction

As a highly active area of research over the past decade, crystal engineering[1] promises the development of new materials based on the structural control of crystalline phases.[2] Organic molecular crystals, based on classical supramolecular interactions, have been recognised as excellent candidates for implementation in optics,[3] gas sorption[4] and catalysis.[5] The class of materials known either as ''coordination polymers'' or ''metal–organic frameworks'' (MOFs) utilise more controllable coordination bonds between (mostly) transition metals and organic ligands for the assembly of materials with varied applications[1h] such as gas sorption,[1d,f,6] separation[2b,7] and sensing[8] as well as catalysis.[2b] We are interested in combining certain features of these two types of materials in order to assemble porous systems based on coordination bonds and molecular packing (*i.e.* coordination bonds are used to control the shape of discrete complexes that might then pack inefficiently). In this regard we have focussed much of our attention on the formation of coordination macrocycles.[8b,9]

We recently reported the X-ray diffraction analysis of a discrete dinuclear metallocycle formed by the mutual coordination of two 1,4-bis[(2-methylimidazol-1-yl)methyl]benzene ligands (**L**) to two copper metal centres (Scheme 1).[8b] The formation of the cyclic structure is presumably guest-templated and the guest solvent molecules are situated within the orifice of the complex where they play a space filling role. Single-crystal to single-crystal transformations occur as a result of removal or exchange of the included guest, with concomitant changes in the conformation of the metallocycle. These transformations seem to indicate that the host is capable of sensing a change in the shape and electrostatic topology of the guest (*i.e.* a conformation change of the host is triggered by subtle supramolecular interactions). Our initial investigation involved formation of the acetone solvate with subsequent replacement of the acetone by acetonitrile as a result of simple immersion in the latter solvent.[8b] We have now extended these studies to investigate the effects of other solvents on the formation of solvent-templated crystals.

Polymorphism of crystals is often influenced by the solvent employed for crystal growth[10] and pseudopolymorphism[11] is always solvent-dependent by definition. The use of different



Scheme 1 Formation of $[Cu_2Cl_4\mathbf{L}_2]\cdot 2$(acetone) where **L** = 1,4-bis[(2-methylimidazol-1-yl)methyl]benzene.

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† Dedicated to Professor George Gokel on the occasion of his 60th birthday.

Table 1 Guest identity, stoichiometry, topology and conformation of structures **1** to **10**

Structure	Guest	Cu : G	Complex type	Conformation	Colour	Stacking pitch[a]/Å	Tilt angle[b]/°	Guest volume/Å^3
1	Acetone	1 : 1	Metallocycle	UUDD	Brown	8.730(1)	49.1	60.6
2	Acetonitrile	1 : 1	Metallocycle	UDDU	Red	8.590(2)	42.5	43.7
3	Dichloromethane	1 : 1	Metallocycle	UUDD	Brown	8.589(3)	49.2	58.4
4	Tetrahydrofuran	1 : 1	Metallocycle	UUDD	Yellow	8.826(3)	49.9	73.2
5	Dimethyl sulfoxide	1 : 1	Metallocycle	UUDD	Brown	8.882(1)	48.8	68.4
6	Ethyl acetate	2 : 1	Metallocycle	UDDU	Red	8.404(2)	42.6	85.8
7	Chloroform	2 : 3	Metallocycle	UDDU	Red	8.132(7)	55.3	74.5
8	1,4-Dioxane	4 : 3	Metallocycle	UUDD and UDDU	Brown	8.601(2)	48.2 and 42.3	81.2
9	1,2-Dichloroethane	1 : 1	1D polymer	—	Yellow	—	—	74.2
10	Dimethylformamide	1 : 2	1D polymer	—	Yellow	—	—	70.7

[a] The stacking pitch determines one of the unit cell axes and is therefore known to a relatively high level of accuracy. [b] The angle between the least-squares plane through the metallocyclic complex and the stacking direction.

solvents, and even combinations of solvents, for the formation of coordination polymers can also result in varying crystal phases.[12] Crystal engineering of coordination polymers is mainly focused on the variation of the organic bridging ligands, the metal ions and the counterions. However, considering the importance of the role of solvent molecules in the crystallisation process, little systematic work has been undertaken in order to address the influence of solvent templation.

In this contribution we present the formation of what may arguably be classed as pseudopolymorphs of a particular combination of metal salt and ligand. The overall aim of our project is to assemble solvent-templated systems that survive solvent removal to yield porous materials. In particular, our strategy is to form "doughnut-shaped" molecules or complexes that stack to form infinite one-dimensional guest-accessible channels through their centres. Therefore it is of considerable importance for us to be conscious of the effect of different solvents on the shapes and packing arrangements of the complexes. We note that, owing to the flexibility of its two methylene linkages, ligand **L** can assume either an approximate C or S shape.

Results and discussion

Crystal growth

The synthesis of the ditopic ligand 1,4-bis[(2-methylimidazol-1-yl)methyl]benzene (**L**) has been described elsewhere.[8b] All crystals of which the structures are presented here were prepared using the same general method. The first stage involved precipitation of the previously reported[8b] $[Cu_2Cl_4\mathbf{L}_2]\cdot 2$(acetone) adduct from an equimolar solution of $CuCl_2\cdot 2H_2O$ and **L** in acetone. These crystals were harvested and dried *in vacuo* to remove the acetone solvent, thus yielding a complex with a precise metal to ligand stoichiometry of 1 : 1 (we have already noted that the metal : ligand ratio can markedly influence the result).[13] A series of eight crystalline solvates was then prepared by dissolving approximately 50 mg of the $[Cu_2Cl_4\mathbf{L}_2]$ complex in *ca.* 5 ml of the appropriate solvent. Each solution was allowed to crystallise by slow evaporation over a period of several days and crystals suitable for single-crystal X-ray diffraction analysis‡ were obtained in all cases.

‡ All structures presented here were determined using single-crystal X-ray diffraction analysis. Phase purity of the contents of each vial was not verified by powder diffraction.

Crystal structures

In all cases X-ray diffraction analysis proved to be unambiguous and no further analytical techniques were deemed necessary to verify the constituents of the crystals. All eight structures have in common that the metal to ligand ratio is 1 : 1, each copper ion is coordinated to two ligands and two chloride ions, and each ligand is coordinated to two copper ions *via* the 3-nitrogen atoms of its two imidazole groups. The host components of the solvated structures consist either of neutral dinuclear metallocyclic complexes with the formula $[Cu_2Cl_4\mathbf{L}_2]$, or one-dimensional polymeric chains with the formula $[CuCl_2\mathbf{L}]_\infty$. It is convenient in the discussion that follows to refer to the former as **A**. Pertinent information relevant to each structure is given in Table 1 which also includes the previously reported structures of **A**·acetone and **A**·acetonitrile. Since a simple molecular formula for a polymeric host can be ambiguous, Cu : guest rather than host : guest ratios are provided in the table. However, in the discussion that follows, the host compound in structures **1** to **8** is conveniently defined as the entire $[Cu_2Cl_4\mathbf{L}_2]$ metallocyclic complex. Structures **1** to **8** share many similarities in molecular conformation and packing modes and it is therefore worthwhile to compare the various structures with respect to the parameters listed in Table 1.

A·2(CH$_3$)$_2$CO (1)

Each copper ion is in a tetrahedrally-distorted square planar coordination environment. Ligand **L** assumes the C-conformation and is coordinated to two metal ions at its opposite ends. A second ligand **L** is also coordinated to the same two metal ions to form a metallocyclic ring as shown in Scheme 1. The molecule is situated on a crystallographic inversion centre and the asymmetric unit consists of half a complex and one acetone molecule. We have already noted that the positions of the four 2-methyl groups on the imidazole rings relative to the mean plane of the metallocycle can be used to describe the overall conformation of the dinuclear complex (Fig. 1): when the complex is viewed perpendicular to its mean plane with the metal···metal axis oriented vertically, we assign the four methyl groups as being directed either up (U) or down (D)

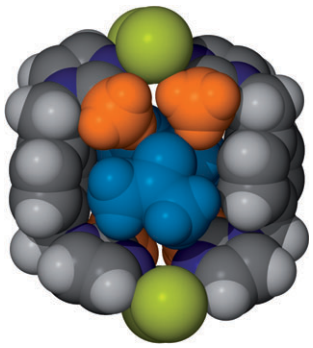

Fig. 1 Space filling representation of the structure of **A** · acetone$_2$ showing the UUDD orientations of the 2-methyl groups (orange) of the imidazole moieties. Guest acetone molecules (light blue) occupy the space within the doughnut-shaped complex. Other colours: carbon, grey; hydrogen, white; nitrogen, dark blue; chloride: yellow.

with respect to the mean plane. We begin by assigning the methyl group at the upper left corner and proceed in a clockwise direction. Using this convention, the complex in **1** is assigned the conformation UUDD.

The overall packing arrangement of the metallocyclic compounds is shown in Fig. 2. The rings are eclipsed along [100] to form columns while the "holes" of the stacked "molecular doughnuts" combine to form solvent channels. Each column is surrounded by six identical columns in an arrangement reminiscent of hexagonal packing of tubes. All neighbouring columns interact with one another by means of weak π–π interaction between phenylene and imidazole rings. Columns adjacent to one another in the direction parallel to [010] consist of complexes in the same orientation within the crystal. However, columns neighbouring one another along [011] are related to one another by 2_1 screw axes and *c*-glide planes and are therefore not similarly oriented. Within each column the stacking repeat distance is equal to the crystallographic *a* axis, *i.e.* 8.730(1) Å. Furthermore, each ring is canted such that the angle between its mean plane and the stacking direction is approximately 49.1° (Fig. 3).[14–16] It is also evident from Fig. 3 that the acetone guest molecules occupy a significant proportion of the solvent-accessible channel and the most significant

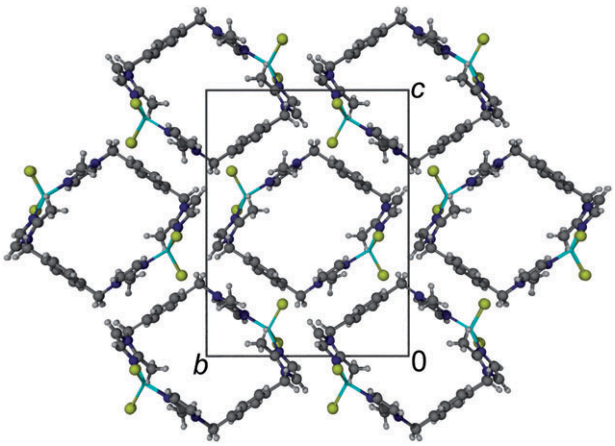

Fig. 2 Ball-and-stick projection of **1** viewed along [100].

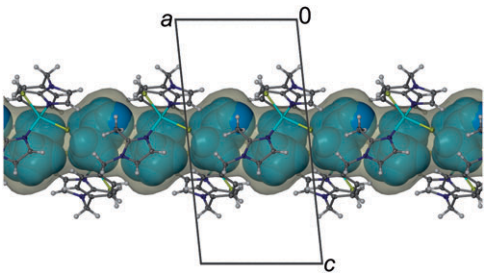

Fig. 3 Projection of **1** viewed perpendicular to (010). The solvent channel passing through the stacked metallocycles is shown as a semitransparent accessible surface (probe radius = 1.5 Å). Projection of the acetone oxygen atoms beyond the accessible surface is due to the formation of C–H···O hydrogen bonds between host and guest. See ref. 14.

host–guest interaction appears to be a single-acceptor bifurcated C–H···O···H–C hydrogen bond (C···O = 3.276(4) and 3.279(4) Å) between two methyl groups of **L** and the carbonyl oxygen atom of the acetone.

A · 2CH$_3$CN (2)

Unlike structures **3** to **10**, **2** was prepared by means of a single-crystal to single-crystal solvent-exchange process. Single crystals of **1** were either immersed in liquid acetonitrile or exposed to acetonitrile vapour for 15 minutes to afford **2**. The two acetone guest molecules originally situated in the molecular cleft of **A** are replaced by two molecules of acetonitrile, as confirmed by X-ray diffraction analysis. The host molecule undergoes a change of conformation which is accompanied by a change in colour from light brown to red. Remarkably, the bulk integrity of the single crystal is maintained despite a relatively large change in the conformation of **A** to UDDU (Fig. 4). This conformation is also centrosymmetric and the space group symmetry is maintained on conversion of **1** to **2**. The stacking periodicity along [100] decreases from 8.730(1)Å in **1** to 8.590(2) Å in **2** with concomitant adjustment of the tilt angle relative to this direction from 49.1° to 42.5°. Notably, the guest-accessible volume (defined using a probe of radius

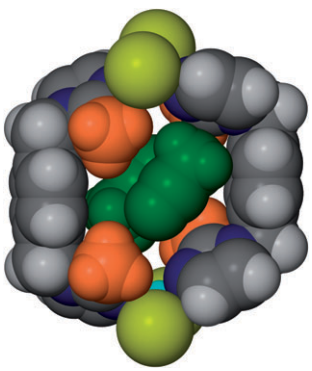

Fig. 4 Space filling representation of the structure of **A** · acetonitrile$_2$ showing the UDDU orientations of the 2-methyl groups (orange) of the imidazole moieties. Guest acetonitrile molecules (green) occupy the space within the doughnut-shaped complex.

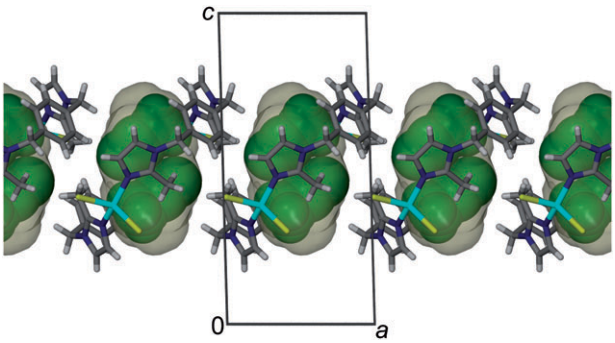

Fig. 5 Projection of **2** viewed perpendicular to (010). The acetonitrile solvent molecules are situated in discrete pockets (semitransparent surface, probe radius = 1.5 Å) within the stacked metallocycles.

1.5 Å) can be described as consisting of discrete pockets of approximately 190 $Å^3$ rather than as infinite channels (Fig. 5).

A · $2CH_2Cl_2$ (3)

The structure of **3** is remarkably similar to that of **1** (see Table 1) and requires little further discussion. The dichloromethane molecules are situated in approximately the same positions relative to the host as observed for the acetone guest molecules of **1**. The host molecules also assume the UUDD conformation.

A · $2C_4H_8O$ (4)

The host conformation of **4** is UUDD and the structure is similar to those of **1** and **3**. However, there is a significant difference in that the THF molecules are weakly coordinated to the copper ions (Cu···O distance = 2.833(3) Å) as shown in Fig. 6. Guest channels running parallel to [100] and passing through the metallocycles are once again evident.

A · $2C_2H_6OS$ (5)

The structure of **5** (Fig. 7) is similar to that of 4 although the guest···copper coordination is much stronger in the former (Cu···O = 2.368(3)Å). The coordination geometry of the copper ion is now trigonal bipyramidal with two ligands **L** in apical positions and the chloride ions and DMSO molecule in axial positions.

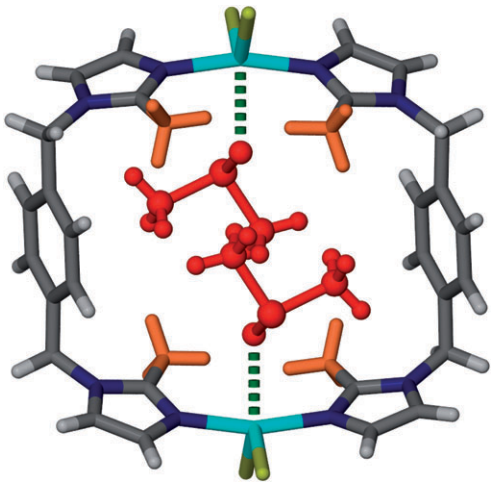

Fig. 7 Structure of **5** showing the UUDD orientation of the methyl groups of the metallocycle. Guest DMSO (red) molecules are interacting with the copper centres (fragmented green bonds).

A · $C_4H_8O_2$ (6)

The conformation of the host is UDDU and the structure is highly reminiscent of that of **2**. The most striking difference between **6** and **2** is that the host : guest ratio of the latter is 1 : 2 while that of **6** is 1 : 1. This is easily rationalised since the volume of ethyl acetate is almost exactly twice that of acetonitrile (Table 1). The guest ethyl acetate is disordered over two positions (Fig. 8) within the host and there appears to be a relatively weak hydrogen bonded interaction between the carbonyl group of the ethyl acetate and a methyl group of the host (O···C = 3.482(5) Å). As noted for **2**, the guest molecules are situated in discrete pockets of approximately 180 $Å^3$ (Fig. 9) rather than in continuous channels.

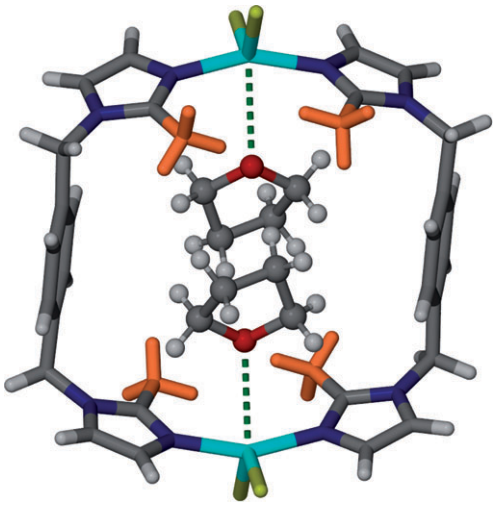

Fig. 6 Structure of **4** showing the UUDD orientation of the methyl groups of the metallocycle. Guest THF molecules are interacting with the copper centres (fragmented green bonds).

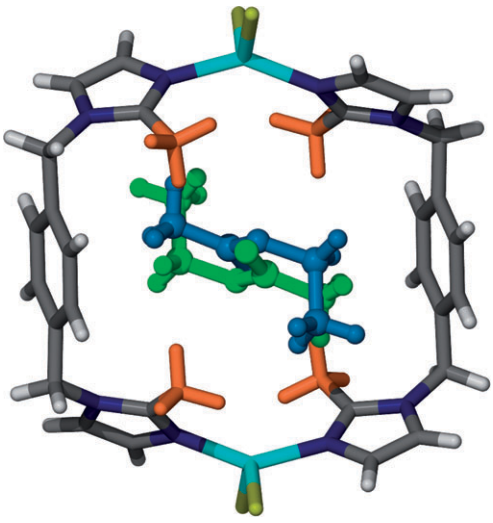

Fig. 8 Structure of **6** showing the UDDU orientation of the methyl groups of the metallocycle. Guest ethyl acetate molecules are disordered over two positions (shown in green and blue).

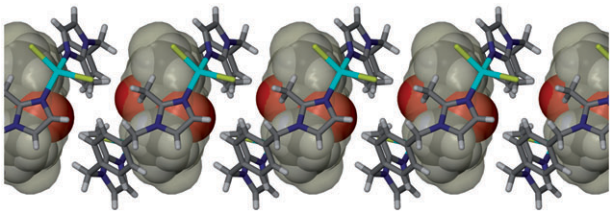

Fig. 9 Projection of **6** viewed perpendicular to (010). The ethyl acetate solvent molecules are situated in discrete pockets (semitransparent surface, probe radius = 1.5 Å) within the stacked metallocycles.

A · 3CHCl$_3$ (7)

The asymmetric unit of **7** consists of one quarter of a metallocyclic complex situated on a 2/*m* symmetry site and a total of three quarters of a chloroform molecule. The final model contains two crystallographically unique chloroform molecules. Both are situated on the mirror plane at *x*,0,*y*. However, one of the guest molecules is also symmetrically disordered across an inversion centre at $\frac{1}{2}$,0,$\frac{1}{2}$.

Although the conformation with regard to the orientation of the imidazole moieties of **A** in **7** is the same as that in **2**, the orientations of the phenylene spacer groups are quite different (Fig. 10). In **2** the phenylene rings are almost vertical (*ca.* 88°) with respect to the plane of the complex whereas the analogous dihedral angle in **7** is *ca.* 17°. As a result of the flattening of the phenylene rings with respect to the complex ring, the aperture through the complex is small and the chloroform guest molecules are situated above and below the plane of the metallocycle.

The stacking repeat distance (*i.e.* 8.132(7) Å along [001]) of the metallocycles in **7** is the shortest of the structures **1** to **8**, but not markedly so. Although the complexes still stack in an eclipsed fashion with a tilt angle of 55.3°, the structure cannot be described as having solvent channels along the host stacking direction. As shown in Fig. 11, the chloroform molecules are too large to be lodged within the host apertures and, indeed, there are two crystallographically unique types of guest molecules. Some of the guests are situated above and below the planes of the complexes as describe above, but the crystallographically unrelated guests (shown in pink) are situated between complexes. Indeed, the guest molecules are

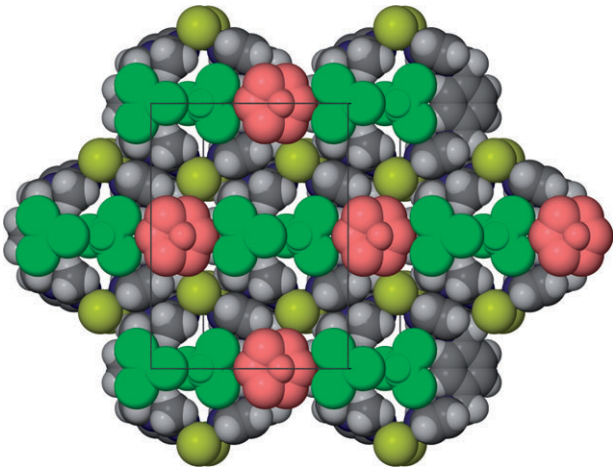

Fig. 11 Space filling projection of **7** viewed perpendicular to (110). Crystallographically unique chloroform molecules are shown in light green and pink.

in van der Waals contact with one another and are located in one dimensional "grooves" parallel to [100].

A$_2$ · 3C$_4$H$_8$O$_2$ (8)

The structure of **8** is the most intriguing of all since it features both the UUDD and UDDU conformations of the metallocyclic complex simultaneously (Fig. 12). The asymmetric unit consists of two unique half molecules of **A**, each situated about an inversion centre. Furthermore, one of these fragments (belonging to the molecule with the UUDD conformation) is associated with one molecule of 1,4-dioxane which is situated close to the inversion site and the other (UDDU) is associated with half a guest molecule situated on an inversion site. Overall, the host : guest geometry is 2 : 3.

Both conformations stack parallel to [100]. However, neither conformation yields a continuous channel. An analysis of the guest-accessible volume (Fig. 13) reveals that the molecules with the UUDD conformation and two guest molecules per host form guest pockets of approximately 246 Å^3. The UDDU host molecules, with only one guest per host, form guest pockets of approximately 135 Å^3. Only weak

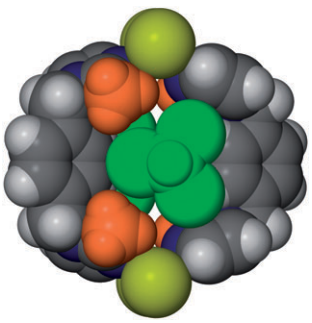

Fig. 10 Space filling projection of **7** showing the UDDU conformation of the host and the relative position of the non-disordered chloroform guest.

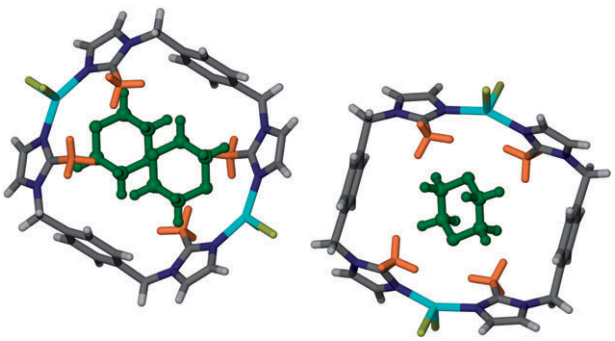

Fig. 12 Projection of **8** showing both UUDD and UDDU conformations present in the same crystal. One of the molecules (UUDD) encircles two dioxane molecules while the other (UDDU) only encircles one.

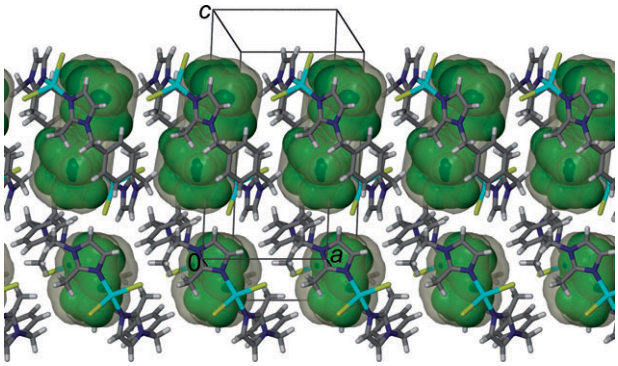

Fig. 13 Projection of **8** showing the formation of two types of guest pockets that accommodate either one or two guest molecules each.

Cu···O(dioxane) interactions of 2.942 and 3.174 Å are evident and presumably play an orientational role with regard to the guest molecules.

1,2-Dichloroethane solvate (9)

Crystallisation from 1,2-dichloroethane results in the formation of a one-dimensional wave-like polymeric compound (Fig. 14). Superficially it seems that this structure might have little in common with those of **1** to **8** since ring-closure does not occur. However, the coordination geometry of the copper ions is still tetrahedrally distorted square planar with the ligands **L** *trans* to one another. Furthermore, the wave-like strands running parallel to [−101] form semi-circular apertures that are closed by the packing of adjacent strands along [010]. The waves stack one over the other along [100] with a repeat distance of 8.539(5) Å, which is highly comparable to those of the cyclic structures. Instead of channels along [100], guest pockets of approximately 143 $Å^3$ are formed (Fig. 15), and each pocket is occupied by only one guest molecule.

Dimethylformamide solvate (10)

DMF is a polar solvent with the ability to coordinate to copper ions. This molecule is also approximately the same size (volume) as 1,2-dichloroethane. Crystallisation from DMF results in the formation of a one-dimensional polymeric strand (Fig. 16). The asymmetric unit consists of one copper(II) ion, two chloride ions, one ligand and two molecules of DMF. One of the DMF molecules coordinates to the copper ion which is in an approximately trigonal bipyramidal environment. Two ligands **L** assume the apical positions while the chloride ions and the coordinated DMF molecule occupy the three equatorial positions. Coordination of the solvent to the metal centre disrupts the geometry about the copper ion relative to structures **1** to **9**. The structure of **10** is therefore of little interest with the exception of demonstrating the effect of a coordinating solvent on the overall structural topology.

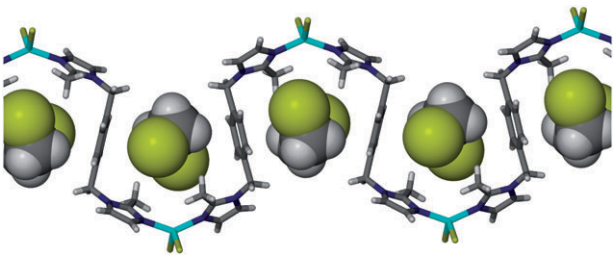

Fig. 14 Wave-like strand formed by the one-dimensional coordination polymer of **9**.

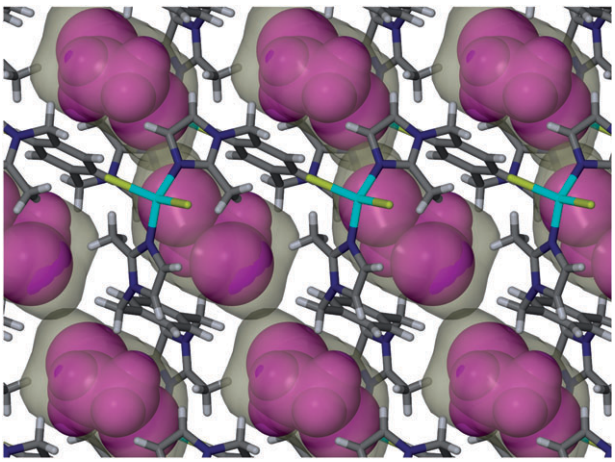

Fig. 15 Guest pockets in **9**. Each pocket is occupied by one molecule of 1,2-dichloroethane (purple, space-filled).

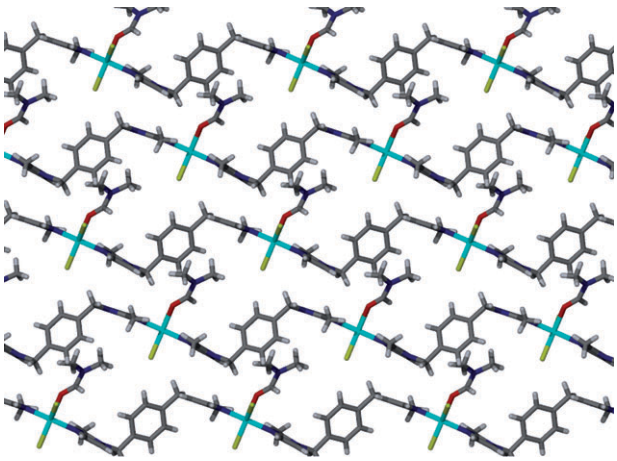

Fig. 16 One-dimensional strands in **10**.

Conclusions

In summary, two types of metallocycles can be identified and they can best be described with reference to the orientations of the methyl groups on the coordinating imidazole moieties relative to the mean plane of the complex. In all of the structures **1** to **8** the stacking is similar: rings are canted at an angle of either *ca.* 42° or 49° relative to a particular axis along which they are stacked, one over the other. This results in the formation either of channels or of discrete pockets in which the guest solvent molecules are situated. The structures consisting of exclusively UUDD conformations form channels while those containing UDDU conformations (or, in one case, a mixture of the two) form solvent-filled cavities. The conformation that results is clearly dependent on the solvent trapped as the guest and, indeed, is most likely solvent-

templated.[17] The UUDD conformations allow far more space for solvent molecules than do the UDDU conformations.

Taken together, the structures presented here represent variation of a range of factors that are known to influence molecular conformation and packing. For example, we have used solvents of different size, shape and electrostatic topology. Furthermore, some solvents are capable of coordinating to the metal or of acting as weak C–H···O hydrogen bond acceptors. However, no clear pattern has emerged that might allow us to predict the conformation, given the identity of the solvent. DMF molecules coordinate to the copper ions and thus cause the formation of one-dimensional polymers rather than discrete metallocycles. On the other hand, THF and DMSO molecules also coordinate to the metals and do not disrupt the formation of cyclic complexes. We also note that formation of wave-like coordination polymers does not preclude packing that is still reminiscent of the stacking of metallocycles with regard to the mode of guest inclusion.

Ultimately, we have shown that this particular system constructed from a 1 : 1 ratio of $CuCl_2$ and **L** can crystallise to give a variety of related structures. Although each structure responds to the nuances imposed by the solvent molecules, we obtain similar structures (in principle) repeatedly in most cases. Indeed, the propensity of a particular host system to favour a particular packing mode is common in supramolecular chemistry and we have already proposed use of the term "isoskeletal" in such cases.[18]

Experimental

Crystal data for 1

$C_{38}H_{48}Cl_4Cu_2N_8O_2$, $M = 917.72$, brown plate, 0.24 × 0.18 × 0.14 mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.7300(13)$, $b = 13.374(2)$, $c = 17.707(3)$ Å, $\beta = 95.956(3)^\circ$, $V = 2056.2(5)$ Å^3, $Z = 2$, $D_c = 1.482$ g cm^{-3}, $F_{000} = 948$, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.6^\circ$, 12 457 reflections collected, 4747 unique ($R_{int} = 0.0426$). Final GooF = 1.027, $R1 = 0.0521$, $wR2 = 0.1197$, R indices based on 3660 reflections with $I > 2\sigma(I)$ (refinement on F^2), 248 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.338$ mm^{-1}. For further information see ref. 8*b*.

Crystal data for 2

$C_{36}H_{42}Cl_4Cu_2N_{10}$, $M = 883.68$, red plate, 0.24 × 0.18 × 0.14 mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.590(2)$, $b = 12.854(3)$, $c = 18.163(4)$ Å, $\beta = 91.596(4)^\circ$, $V = 2004.8(8)$ Å^3, $Z = 2$, $D_c = 1.464$ g cm^{-3}, $F_{000} = 908$, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.0^\circ$, 8012 reflections collected, 4213 unique ($R_{int} = 0.1185$). Final GooF = 1.084, $R1 = 0.1044$, $wR2 = 0.1959$, R indices based on 2245 reflections with $I > 2\sigma(I)$ (refinement on F^2), 238 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.368$ mm^{-1}. For further information see ref. 8*b*.

Crystal data for 3

$C_{34}H_{40}Cl_8Cu_2N_8$, $M = 971.42$, brown plate, 0.23 × 0.14 × 0.01 mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.598(3)$, $b = 13.177(4)$, $c = 18.105(6)$ Å, $\beta = 95.181(6)^\circ$, $V = 2042.9(11)$ Å^3, $Z = 2$, $D_c = 1.579$ g cm^{-3}, $F_{000} = 988$, Bruker APEX CCD area-detector, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.5^\circ$, 12 610 reflections collected, 4733 unique ($R_{int} = 0.0900$). Final GooF = 0.966, $R1 = 0.0620$, $wR2 = 0.1108$, R indices based on 2851 reflections with $I > 2\sigma(I)$ (refinement on F^2), 237 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.601$ mm^{-1}. CCDC reference number 635644. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618495m

Crystal data for 4

$C_{40}H_{52}Cl_4Cu_2N_8O_2$, $M = 945.78$, yellow block, 0.12 × 0.09 × 0.07 mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.826(3)$, $b = 13.103(5)$, $c = 18.057(6)$ Å, $\beta = 95.838(7)^\circ$, $V = 2077.5(12)$ Å^3, $Z = 2$, $D_c = 1.512$ g cm^{-3}, $F_{000} = 980$, Bruker APEX CCD area-detector, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 50.2^\circ$, 10 633 reflections collected, 3662 unique ($R_{int} = 0.1379$). Final GooF = 1.059, $R1 = 0.0908$, $wR2 = 0.1486$, R indices based on 2235 reflections with $I > 2\sigma(I)$ (refinement on F^2), 255 parameters, 42 restraints. Lp and absorption corrections applied, $\mu = 1.327$ mm^{-1}. CCDC reference number 635645.

Crystal data for 5

$C_{36}H_{48}Cl_4Cu_2N_8O_2S_2$, $M = 957.82$, brown block, 0.19 × 0.17 × 0.15 mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.8822(14)$, $b = 13.050(2)$, $c = 17.792(3)$ Å, $\beta = 95.486(3)^\circ$, $V = 2052.9(6)$ Å^3, $Z = 2$, $D_c = 1.550$ g cm^{-3}, $F_{000} = 988$, Bruker APEX CCD area-detector, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.5^\circ$, 12 572 reflections collected, 4724 unique ($R_{int} = 0.0527$). Final GooF = 1.033, $R1 = 0.0516$, $wR2 = 0.1074$, R indices based on 3599 reflections with $I > 2\sigma(I)$ (refinement on F^2), 248 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.442$ mm^{-1}. CCDC reference number 635646.

Crystal data for 6

$C_{36}H_{44}Cl_4Cu_2N_8O_2$, $M = 889.67$, red block, 0.13 × 0.11 × 0.07 mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.4038(15)$, $b = 12.927(2)$, $c = 18.195(3)$ Å, $\beta = 91.267(3)^\circ$, $V = 1976.2(6)$ Å^3, $Z = 2$, $D_c = 1.495$ g cm^{-3}, $F_{000} = 916$, Bruker APEX CCD area-detector, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.6^\circ$, 10 921 reflections collected, 4464 unique ($R_{int} = 0.0614$). Final GooF = 1.153, $R1 = 0.0721$, $wR2 = 0.1311$, R indices based on 3240 reflections with $I > 2\sigma(I)$ (refinement on F^2), 266 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.390$ mm^{-1}. CCDC reference number 635647.

Crystal data for 7

$C_{35}H_{39}Cl_{13}Cu_2N_8$, $M = 1159.67$, red block, 0.30 × 0.20 × 0.20 mm^3, monoclinic, space group $C2/m$ (No. 12), $a = 15.700(13)$, $b = 21.205(18)$, $c = 8.132(7)$ Å, $\beta = 121.048(13)^\circ$, $V = 2320(4)$ Å^3, $Z = 2$, $D_c = 1.660$ g cm^{-3}, $F_{000} = 1168$, Bruker APEX CCD area-detector, MoKα radiation, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $2\theta_{max} = 50.2^\circ$, 4230 reflections collected, 2043 unique ($R_{int} = 0.1316$). Final GooF = 0.955, $R1 = 0.0824$, $wR2 = 0.1724$, R indices based on 1016 reflections with

$I > 2\sigma(I)$ (refinement on F^2), 145 parameters, 2 restraints. Lp and absorption corrections applied, $\mu = 1.704$ mm^{-1}. CCDC reference number 635648.

Crystal data for 8

$C_{76}H_{96}Cl_8Cu_4N_{16}O_6$, $M = 1867.45$, brown plate, 0.31 × 0.14 × 0.02 mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.6006(17)$, $b = 13.126(3)$, $c = 17.942(4)$ Å, $\alpha = 87.547(4)$, $\beta = 87.705(4)$, $\gamma = 81.627(4)^\circ$, $V = 2000.9(8)$ Å^3, $Z = 1$, $D_c = 1.550$ g cm^{-3}, $F_{000} = 964$, Bruker APEX CCD area-detector, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.7^\circ$, 23 305 reflections collected, 9260 unique ($R_{int} = 0.0856$). Final GooF = 1.116, $R1 = 0.0879$, $wR2 = 0.1568$, R indices based on 6320 reflections with $I > 2\sigma(I)$ (refinement on F^2), 500 parameters, 39 restraints. Lp and absorption corrections applied, $\mu = 1.379$ mm^{-1}. CCDC reference number 635649.

Crystal data for 9

$C_{18}H_{22}Cl_4CuN_4$, $M = 499.74$, yellow prism, 0.24 × 0.19 × 0.14 mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.539(5)$, $b = 10.673(6)$, $c = 13.386(7)$ Å, $\alpha = 104.272(10)$, $\beta = 91.858(10)$, $\gamma = 112.793(9)^\circ$, $V = 1078.7(10)$ Å^3, $Z = 2$, $D_c = 1.539$ g cm^{-3}, $F_{000} = 510$, Bruker APEX CCD area-detector, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.6^\circ$, 6815 reflections collected, 4785 unique ($R_{int} = 0.0517$). Final GooF = 0.959, $R1 = 0.0731$, $wR2 = 0.1420$, R indices based on 2940 reflections with $I > 2\sigma(I)$ (refinement on F^2), 246 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.519$ mm^{-1}. CCDC reference number 635650.

Crystal data for 10

$C_{22}H_{32}Cl_2CuN_6O_2$, $M = 546.98$, yellow block, 0.23 × 0.18 × 0.12 mm^3, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.8579(11)$, $b = 14.7460(13)$, $c = 13.8823(12)$ Å, $\beta = 98.669(2)^\circ$, $V = 2602.0(4)$ Å^3, $Z = 4$, $D_c = 1.396$ g cm^{-3}, $F_{000} = 1140$, Bruker APEX CCD area-detector, MoKα radiation, $\lambda = 0.71073$ Å, $T = 303(2)$ K, $2\theta_{max} = 56.6^\circ$, 16 123 reflections collected, 5982 unique ($R_{int} = 0.0555$). Final GooF = 1.015, $R1 = 0.0837$, $wR2 = 0.1932$, R indices based on 3428 reflections with $I > 2\sigma(I)$ (refinement on F^2), 304 parameters, 39 restraints. Lp and absorption corrections applied, $\mu = 1.075$ mm^{-1}. CCDC reference number 635643.

Acknowledgements

We thank the National Research Foundation of South Africa for financial support of this project. LD also thanks the Claude Leon Foundation for financial support in the form of a postdoctoral fellowship.

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