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Copper(I) dicyanamide coordination polymers: ladders, sheets, layers, diamond-like networks and unusual interpenetration†

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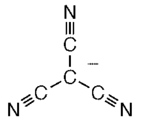
The structures of six new derivatives of copper(I) dicyanamide (dicyanamide = $N(CN)_2^-$, dca) have been determined. Those of Cu(dca)(MeCN) **1** and $Cu(dca)(Me_4pyz)_{1/2}$ **2**, Me_4pyz = tetramethylpyrazine, both contain (6,3) sheets. $Cu_2(dca)_2(bipy)(MeCN)_2\cdot0.5bipy$ **3**, bipy = 4,4′-bipyridine, consists of 1-D ladder-like polymers with intercalated bipy guests. $Cu_4(dca)_4(bipy)_3(MeCN)_2$ **4** is composed of 2-D layers which each interpenetrate with four others in a parallel fashion, resulting in a novel 3-D interlocking of layers. α-Cu(dca)(bpe) **5**, bpe = 1,2-bis(4-pyridyl)ethene, consists of 2-D (4,4) sheets displaying twofold parallel interpenetration, while β-Cu(dca)(bpe) **6** contains five diamond-like networks which interpenetrate in an unprecedented fashion.

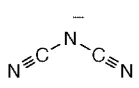
The crystal engineering of coordination polymers is becoming an increasingly popular field of research,[1–3] and offers the promise of deliberately designing new materials with useful properties such as microporosity, molecular magnetism or non-linear optical behaviour. By controlling the favoured geometry of ligands and metals we can influence the topology of the resultant polymeric network. Many new and exciting structures have been reported, often displaying beautiful and intricate entanglement of multiple networks (interpenetration).[4]

We have been looking at the coordination polymers formed by the pseudohalide ligands tricyanomethanide (tcm, $C(CN)_3^-$) and dicyanamide (dca, $N(CN)_2^-$). In particular, we recently reported the structures of three closely related polymers, Cu(tcm)(hmt), Cu(tcm)(bipy) and $[Cu(tcm)(bpe)]\cdot0.25bpe\cdot0.5MeCN$, hmt = hexamethylenetetramine, bipy = 4,4′-bipyridine, bpe = 1,4-bis(4-pyridyl)ethene.[5] These three compounds formed a very interesting series because although they all contained (4,4) Cu(tcm)(L) sheets, they each used a different method of maximising the packing efficiency of their structures, displaying interdigitation, interpenetration and intercalation, respectively. As the tcm ligand in these three compounds coordinated through only two of the three nitrile groups, we were interested in the dca analogues of these materials, expecting them to show similar structures. We report here the results of these investigations. A number of other interesting compounds of copper(I) halides or pseudohalides with bridging pyridyl-donor co-ligands have also been reported.[2,6]

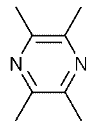
Dicyanamide has also attracted a great deal of interest of late due to the long-range magnetic ordering observed in some of its coordination polymers. The α-$M(dca)_2$ series of compounds, which have isomorphous rutile-like structures, display ferromagnetism (Co ($T_c = 9$ K), Ni (20 K)), spin-canted anti-ferromagnetism (Cr ($T_N = 47$ K), Mn (16 K), Fe (19 K)) and paramagnetism (Cu).[7] The unusual magnetic properties of these compounds has led to the characterisation of a large number of new coordination polymers containing the dca ligand. Structures reported recently include $M(dca)_2L_2$ chains, (4,4) sheets, interpenetrating α-Po networks, chains penetrating sheets, molecular tubes and self-penetrating networks.[7,8] In these structures dca adopts two different bridging modes, μ (coordinating through the two nitrile nitrogen atoms) and μ_3 (coordinating through all three nitrogen atoms). A number of other coordination polymers of dca have also been reported some time ago.[9]



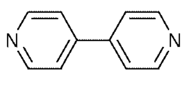
tcm



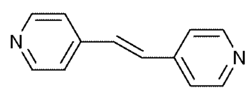
dca



Me₄pyz



bipy



bpe

Results and discussion

Cu(dca)(MeCN) 1

The structure of Cu(dca)(MeCN) consists of buckled (6,3) sheets with alternating 3-connecting copper atoms and dca ligands (Fig. 1). The geometry of the copper atoms is in fact tetrahedral, involving three dca ligands (one through an amide nitrogen and two others through nitrile nitrogens) and one terminal acetonitrile ligand. This induces a buckling in the sheets, and the acetonitrile ligands are directed above and below the sheet in an alternating fashion. The sheets then stack in the *a* direction, with the acetonitrile appendages of adjoining layers interdigitated.

The structure is similar to that of Ag(tcm)(MeCN) (and Ag(tcm) itself).[10] This compound also contains (6,3) sheets composed of alternate 3-connecting ligands and metals, and the geometries are again tetrahedral, with terminal acetonitrile ligands directed above and below the buckled sheets. The tcm ligand, however, contains three long ‘C–CN–Ag’ links between the two 3-connecting nodes of the network, and 2-fold parallel interpenetration occurs. For the dca ligand in Cu(dca)(MeCN), however, there are only two long links of comparable length to those of the silver compound (N–CN–Cu) and one

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Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format and structure diagrams of **1**, **2**, **5** and **6**. See http://www.rsc.org/suppdata/dt/b0/b003527k/

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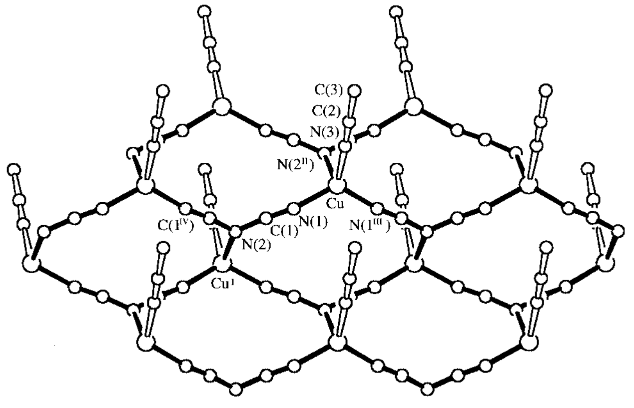

Fig. 1 A single (6,3) sheet in the structure of Cu(dca)(MeCN) **1**, with terminal acetonitrile ligands represented by the open bonds. Selected bond lengths and angles: Cu–N(1) 1.942(1), Cu–N(2^{II}) 2.273(2), Cu–N(3) 1.967(2) Å, Cu–N(1)–C(1) 168.7(1), Cu^{I}–N(2)–C(1) 118.33(9), Cu–N(3)–C(2) 175.0(2)°.

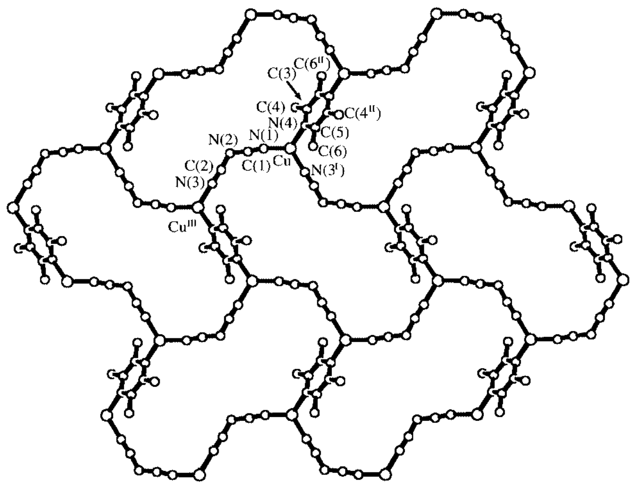

Fig. 2 A single (6,3) sheet in the structure of Cu(dca)(Me$_4$pyz)$_{1/2}$ (**2**). Selected bond lengths and angles: Cu–N(4) 2.005(2), Cu–N(1) 1.911(2), Cu–N(3^{I}) 1.931(2) Å, Cu–N(1)–C(1) 169.2(2), Cu–N(3^{I})–C(2^{I}) 176.4(2)°.

much shorter link (Cu–N). Consequently, the windows in the sheets are much smaller, and interpenetration does not occur. A similar situation is seen in the rutile-like networks of ML$_2$, L = dca or tcm. For tcm, two interpenetrating rutile-like networks are seen,[11] but for dca there is only one rutile-like network.[7] Again, this is due to the shortening of one third of the links between the trigonal nodes from M–NC–C to M–N(amide).

Cu(dca)(Me$_4$pyz)$_{1/2}$ 2

The structure of compound **2** consists of (6,3) sheets, with 3-connecting copper atoms bridged by 2-connecting dca and tetramethylpyrazine (Me$_4$pyz) ligands (Fig. 2). The dca ligands coordinate through the nitrile nitrogens, and the amide nitrogen participates in weak interactions with methyl hydrogens on two nearby Me$_4$pyz ligands (C–H · · · N 146.1, 163.9°; H · · · N 2.657, 2.659 Å; C · · · N 3.513, 3.610 Å, respectively). The sheets are buckled and lie parallel to the (102) plane.

Cu$_2$(dca)$_2$(bipy)(MeCN)$_2$·0.5bipy 3

Reaction of bipy, [PPN][dca] (PPN = bis(triphenylphosphoranylidene)ammonium) and copper(I) perchlorate in acetonitrile gave two different products. In a typical reaction, formation of yellow-orange dichromic crystals (**3**) occurred first. These crystals then redissolved over 1–3 days and dark red crystals (**4**) formed in their place. This is indicative of **3** being a kinetic product of the reaction, and **4** being the more thermodynamically stable phase.

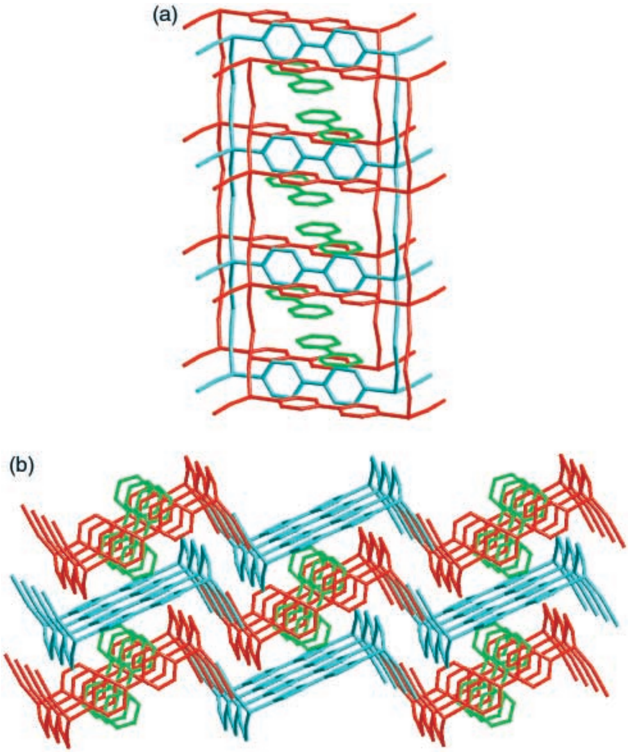

Fig. 3 (a) Intercalation of guest bipy molecules (green) in a single stack of ladders in the structure of Cu$_2$(dca)$_2$(bipy)(MeCN)$_2$·0.5bipy **3**. The bipy guests lie in the windows of one type of ladder (red), and these ladders stack in an alternating fashion with a second type of ladder (blue). Selected bond lengths and angles for red ladders (blue ladders in parentheses): Cu–N(bipy) 2.090(5) (2.088(5)), Cu–N(MeCN) 2.004(4) (1.977(5)), Cu–N(dca) 1.971(3) Å (1.976(4) Å), Cu–N–C(dca) 168.3(3)°(169.7(4)°). (b) Interdigitation of adjacent stacks of ladders in **3**.

The structure of compound **3** consists of stacks of ladder-like 1-D polymers with uncoordinated bipy passing through the windows of the ladders (Fig. 3). A number of other 1-D coordination polymers with similar ladder-type structures have been reported.[12] Copper dicyanamide chains form the two sides of the ladders, and bridging bipy ligands provide the rungs. The ladders stack in columns parallel to the *c* axis, creating square channels due to the overlap of the ladder windows, and the uncoordinated bipy lie in these channels. The tetrahedral geometry of the copper atoms is completed by terminal acetonitrile ligands.

There are two crystallographically unique ladders (shown as red and blue in Fig. 3). These two types of ladders stack in an alternating fashion, and the bipy guests lie in the windows of only one type of ladder (the red ladders). The bipy rungs of these ladders are twisted such that they are exactly perpendicular to the plane of the window. This maximises the size of the window, and allows π–π interactions between the bipy guest molecules and the two bipy rungs on either side (distance between the mean planes is $b/2$ = 3.788 Å). The other types of ladders (the blue ones) do not contain guests, and the bipy rungs lie in the plane of the windows. This reduces the effective size of these windows and allows closer approach of these ladders to the adjoining (red) ladders in the stacks. These stacks of ladders are then assembled in the third dimension such that the acetonitrile appendages are interdigitated, as shown in Fig. 3(b).

Cu$_4$(dca)$_4$(bipy)$_3$(MeCN)$_2$ 4

The structure of compound **4** consists of thick 2-D layers in which buckled (6,3) sheets are coupled together in pairs by

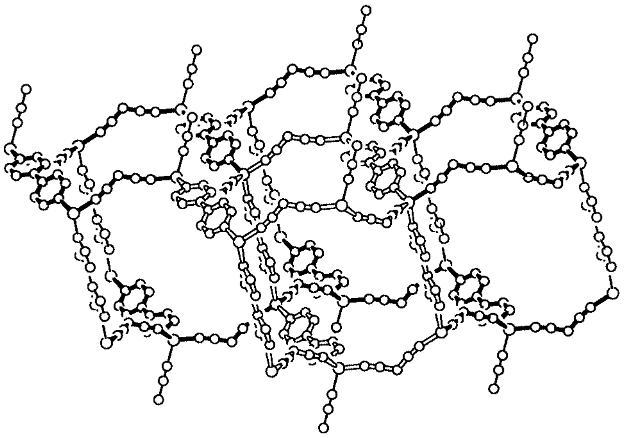

Fig. 4 A single layer in the structure of $Cu_4(dca)_4(bipy)_3(MeCN)_2$ **4**. The terminal acetonitrile ligands and the bipy ligands bridging the two (6,3) sheets (top and bottom) are highlighted by the thin bonds, and a single adamantane unit is also highlighted by the open bonds. Selected bond lengths and angles: Cu–N(bipy) 2.046(2), 2.076(2), 2.088(2), Cu–N(MeCN) 2.017(2), Cu–N(dca) 1.948(2)–1.983(2) Å, Cu–N–C(dca) 154.7(2)–174.8(2) °.

bridging bipy ligands (Fig. 4). The (6,3) sheets, which form the top and bottom of the layers, are composed of copper atoms bridged by bipy and dca ligands. There are two dca ligands for every bipy ligand within the sheets, and they bridge such that the bipy ligands form two opposing sides of the hexagonal rings of the sheets. The geometry of the copper atoms is tetrahedral, involving one bipy and two dca ligands each within the sheets. For every second metal the coordination geometry is completed by terminal acetonitrile ligands, while every other metal atom completes its coordination sphere with a bipy ligand bridging between sheets.

Close inspection of the layers reveals that they are composed of adamantane-like cavities (Fig. 4). In fact, the topology of these layers is such that they represent a 2-D cross-section of the diamond network, one adamantane unit thick, terminated by acetonitrile ligands.

The layers, all of which are equivalent, interpenetrate such that each layer interpenetrates with four other parallel layers. Unlike most other examples of parallel interpenetration of 2-D sheets (including **5**),[4] the mean planes of the interpenetrating layers are parallel but *not* coincident. This means that the interlocking of the layers produces an overall 3-D structure, rather than discrete 2-D layers of interpenetrating sheets.

The interpenetration of three layers is shown schematically in Fig. 5(a). The layers depicted in green and blue penetrate through the top of the red layer. Not shown are two further layers which penetrate through the bottom of the red layer in an identical fashion. Thus each hexagonal window of the (6,3) sheets has two bipy rods, each from a separate layer, passing through it, and each layer interpenetrates with four others. The two layers penetrate the top face at two different 'heights', one with its bottom (6,3) sheet close to the top of the red layer, and one with its bottom (6,3) sheet approximately in the middle of the red layer. This latter blue layer interlocks with the equivalent layer passing through the bottom of the red layer in the same fashion as the red and green layers do in Fig. 5(a).

The effect of the interpenetration of layers with parallel but non-coincident mean planes is shown in Fig. 5(b). An overall 3-D entangled structure results from the interpenetration within the stacking 2-D layers. Note in the Figure that the top, middle and bottom layers (red) are not directly interpenetrating, but are entangled indirectly *via* the other four layers shown, which interpenetrate either both the top and middle layers, or both the middle and bottom layers. As all layers are equivalent, the top (or bottom) sheet of any layer interpenetrates one layer close to the bottom (or top), and another at approximately the middle.

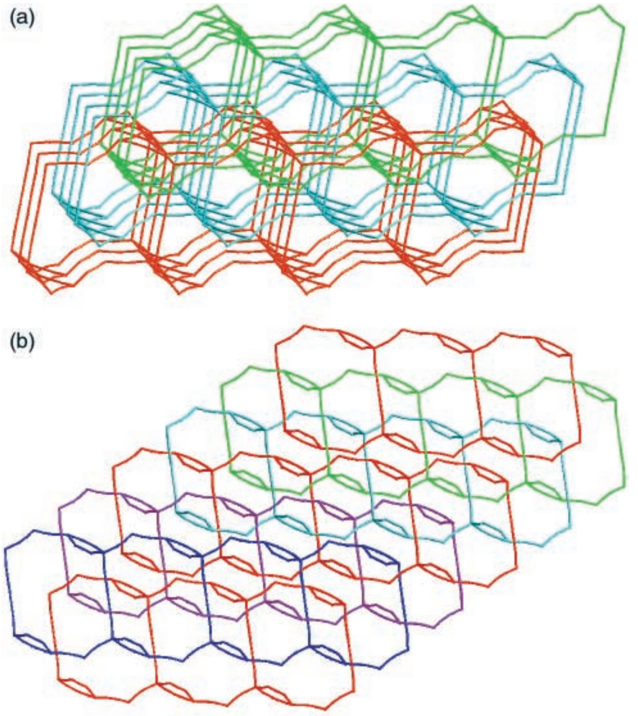

Fig. 5 (a) Interpenetration of two layers (blue and green) at different 'heights' through the top face of a third layer (red) in the structure of compound **4**. For clarity, the acetonitrile ligands are omitted, and the bipy ligands are shown schematically. (b) Seven interpenetrating layers. Note only the four layers interpenetrating the central red layer are shown, as well as the next two layers (red) which are not directly interpenetrating the central layer.

Finally, the acetonitrile appendages of each layer poke through the hexagonal rings in the sheets of those layers which are closest to it but are not *directly* interpenetrating, and *vice versa*. Thus, for example, the red layers in Fig. 5(b) interdigitate in this fashion.

It is interesting that the only difference in the formulae of compounds **3** and **4** is the ratio of solvent to copper—**4** has half the amount of acetonitrile found in **3**. The ratio of copper to dca and bipy is the same in both structures.

Only five other examples of parallel interpenetration generating a 3-D entangled structure are known. The isomorphous structures of $[Ag(sebn)_2]X$, sebn = sebaconitrile, $X = SbF_6^-$ or $CF_3SO_3^-$, contain thick layers similar to those described here, however in these structures each layer is interpenetrated directly with only two other layers.[13] If Ag···Ag contacts are ignored in the isomorphous structures of $[Ag_2(H_2L)_3]X_2$, H_2L = N,N′-bis(salicylidene)-1,4-diaminobutane, $X = NO_3^-$ or ClO_4^-, then they can be considered to consist of (6,3) sheets which interlock in a parallel fashion to generate a 3-D structure.[14] In these structures it is not the 'thickness' of the sheets but the deep corrugation which allows each sheet to be directly interpenetrating two others. Most significantly, the structure of $[Ag_3\{Si(C_6H_4CN\text{-}p)_4\}_2][PF_6]_3$·solv contains thick layers of identical topology to that of **4** which interpenetrate in an identical fashion to that described here.[15]

α-Cu(dca)(bpe) 5

Reaction of bpe, [PPN][dca] and copper(I) perchlorate in acetonitrile resulted in immediate formation of a yellow amorphous precipitate. Crystals of this product could not be obtained, however its IR spectrum indicated the presence of dca and bpe and the absence of ClO_4^-. Following this immediate precipitation of yellow precipitate, orange (**5**) and dark red crystals (**6**) formed. The structures of both these products were

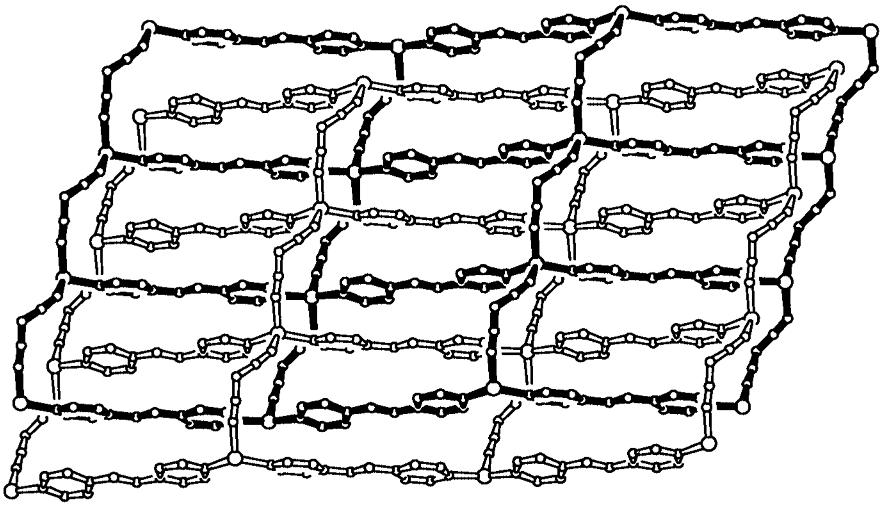

Fig. 6 The twofold parallel interpenetration of (4,4) sheets in α-Cu(dca)(bpe) **5**. Selected bond lengths and angles: Cu–N(bpe) 1.995(2), 2.010(2), Cu–N(dca) 2.005(2), 2.127(2) Å, Cu–N–C(dca) 165.5(2), 132.4(2)°.

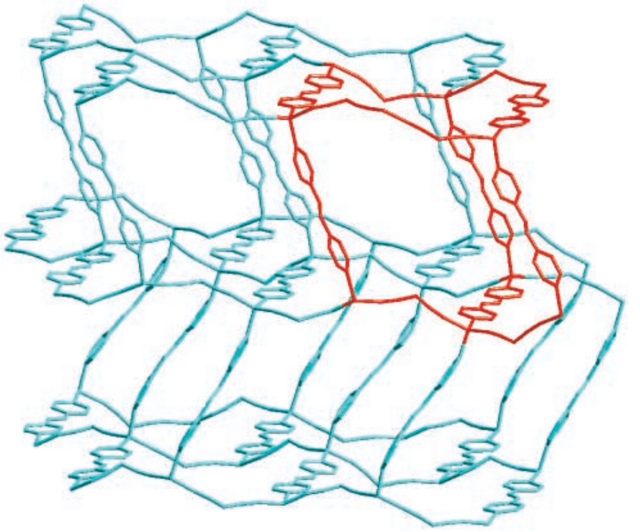

Fig. 7 One diamond-like net in the structure of β-Cu(dca)(bpe) **6**, with a single adamantane highlighted. Ranges for selected bonds lengths and angles: Cu–N(bpe) 2.042(5)–2.125(5), Cu–N(dca) 1.915(5)–2.026(5) Å, Cu–N–C(dca) 150.5(5)–173.6(5)°.

determined crystallographically, and found to have the identical formula Cu(dca)(bpe).

The structure of compound **5** is very similar to that of Cu(tcm)(bipy).[5] It consists of corrugated (4,4) sheets displaying twofold parallel interpenetration (Fig. 6).[4] Collinear tetrahedral Cu atoms are bridged by bent dca bridges parallel to *a*, while linear bpe bridges connect the Cu atoms into zigzag chains parallel to (201), resulting in corrugated sheets. Unlike **4**, in which the interpenetration of 2-D networks gave an overall 3-D structure, in **5** discrete, separate 2-D layers are formed which each contain two interpenetrating sheets. These layers stack along *b*.

The interpenetration is such that the bpe ligands of each net penetrate the $Cu_4(dca)_2(bpe)_2$ windows of the other. This results in a criss-crossing along the *a* direction of bpe ligands from alternating sheets. The criss-crossing bpe ligands are separated by $a/2 = 3.692$ Å.

β-Cu(dca)(bpe) 6

The structure of compound **6** consists of five interpenetrating diamond-like networks. Each network, all of which are equivalent, is composed of tetrahedral Cu atoms bridged by 2-connecting dca and bpe bridges. The structure of a single net is shown in Fig. 7.

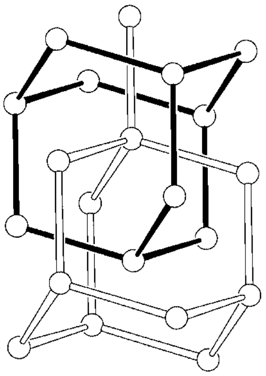

Fig. 8 Two interpenetrating adamantane units, as defined in the text, in the normal mode of interpenetration for diamond-like networks.

Interpenetration of diamond-like nets is the most common form of interpenetration,[4] and in all but one reported case they all show the same mode of interpenetration. To illustrate the unusual interpenetration topology in compound **6** we shall first examine the ‘normal’ mode of interpenetration. The diamond net can be broken down into adamantane-like cavities, which consist of four 6-membered windows. When two or more networks interpenetrate these windows are penetrated by rods from the other networks. We can use this fact to define adamantane units in the interpenetrating networks which have a unique relationship to each other. For two interpenetrating nets, choose any adamantane unit in net 1, choose any one of the four 6-membered windows of this cavity, and then select the unique rod of net 2 which penetrates this window. This rod is a connection between two nodes of net 2; choose the node which is inside the net 1 cavity we have defined, and then construct the unique adamantane unit of net 2 which is defined by the three *remaining* links from this node. This relationship in two networks displaying normal interpenetration is shown in Fig. 8. Note that in normal interpenetration, regardless of the total number of networks, the result for any adamantane unit, and any 6-membered ring, is topologically identical for any two nets selected.

Although all five nets in compound **6** are crystallographically equivalent, the asymmetric unit consists of six Cu atoms, six bpe ligands and six dca ligands, and thus there are a large number of crystallographically unique hexagonal rings and adamantane units. However, as each adamantane unit is interpenetrated in an identical fashion in the normal mode of interpenetration, we need only to show the difference for one adamantane unit in **6** to prove the different mode of interpenetration.

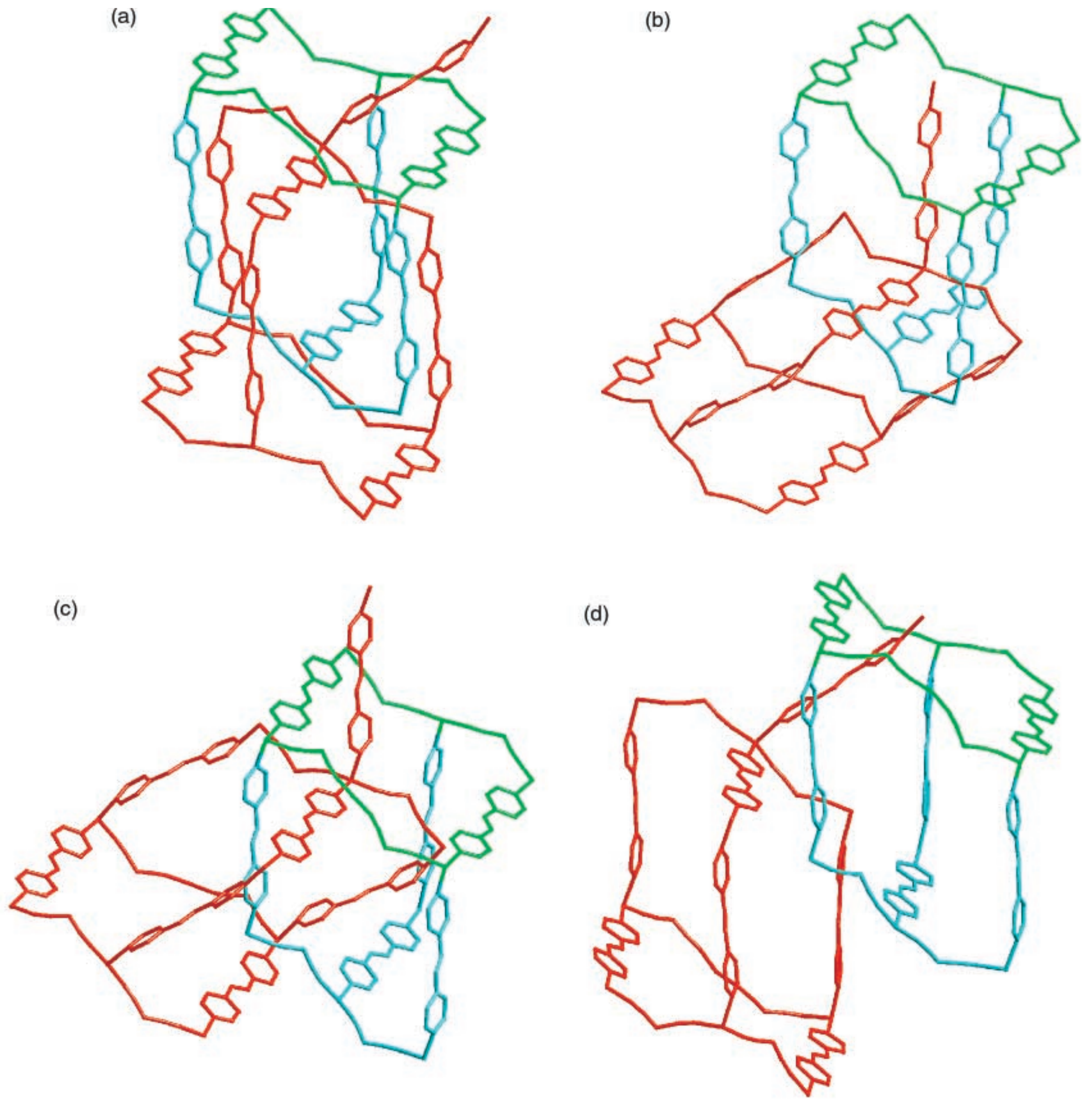

Fig. 9 The relationships of an arbitrary adamantane unit in net 1 (blue/green) to those (shown in red) in (a) net 2, (b) net 3, (c) net 4, and (d) net 5, as defined in the text, in the structure of compound **6**. The 6-membered window of net 1 used to define the other four adamantane units is highlighted in green. In (a) and (b) the mode of interpenetration is the same as shown in Fig. 8, however in (c) and (d) the modes are clearly different. All nets are crystallographically equivalent, and the numbering of the nets is arbitrary.

The complicated relationship between an adamantane unit of one net (net 1; chosen arbitrarily) and those of the four other nets (defined as above) is shown in Fig. 9, with the initial adamantane unit of net 1 shown in blue, and the 6-membered ring chosen shown in green. Nets 2–5 are shown in red in Fig. 9(a)–(d), respectively. As can be seen in Fig. 9(a) and 9(b), the relationships of the net 1 adamantane unit to the net 2 and net 3 adamantane units are as normal. The relationship to net 4 (Fig. 9(c)), however, is different. Instead of the four windows of the net 1 adamantane unit having one rod each from the initial defining node of net 4 passing through them, one window has no rods at all (from this node) passing through it, while another window is penetrated a second time by the net 4 adamantane unit. The relationship to net 5 (Fig. 9(d)) is also different. In this case the initially defined rod of net 5 passes through two 6-membered rings of net 1, and the two adamantane units are not entangled at all; they can be separated without breaking links. In this case two windows of the net 1 adamantane unit are penetrated by a rod (the same rod), while the two other windows are not penetrated at all.

The five hydrogen bonded diamond-like networks of adamantane-1,3,5,7-tetracarboxylic acid reported by Ermer is the only other structure that has been reported with a different mode of interpenetration to the normal mode for diamond networks. In this structure, however, any two nets interpenetrate normally, and only addition of third (and subsequent) nets results in a new interpenetration topology.[4,16]

Conclusion

The six compounds described here were produced from only four simple and closely related reactions and yet display very different and complex structures. The structures were also surprisingly different to those of their Cu(tcm)(L) analogues. This again highlights the difficulty in predicting crystal structures with certainty; many different possibilities can exist even for relatively simple systems such as those described here. Rational selection and design of ligands and metals allow us to direct a reaction along a certain direction, increasing the chances of producing our desired structure, however there are nearly always alternative structures possible, and thus experimental verification of design is both mandatory and liable to produce unexpected surprises. The formation of pseudopolymorphs[17] (**3** and **4**) and true polymorphs (**5** and **6**) illustrated here is an elegant illustration of the challenges faced by crystal engineering.

Nonetheless, the structures presented here show that subtle variation of reagents can have dramatic effects on the structures generated. Simple combinations of ordinary ligands and metals have resulted in some very complex structures of varying

Table 1 Crystallographic data for compounds **1**–**6**

	Cu(dca)(MeCN) **1**	Cu(dca)(Me$_4$pyz)$_{1/2}$ **2**	Cu$_2$(dca)$_2$(bipy)-(MeCN)$_2$·0.5bipy **3**	Cu$_4$(dca)$_4$(bipy)$_3$-(MeCN)$_2$ **4**	α-Cu(dca)(bpe) **5**	β-Cu(dca)(bpe) **6**
Formula	$C_4H_3CuN_4$	$C_6H_6CuN_4$	$C_{23}H_{18}Cu_2N_{11}$	$C_{42}H_{30}Cu_4N_{20}$	$C_{14}H_{10}CuN_5$	$C_{14}H_{10}CuN_5$
M	170.64	197.69	575.56	1069.02	311.81	311.81
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/c$	*C*2/*m*	$P\bar{1}$	$Pna2_1$	*Cc*
a/Å	13.0351(4)	3.8969(1)	29.5142(7)	8.2104(3)	7.3835(1)	12.2904(3)
b/Å	7.7296(2)	18.5279(9)	7.5761(3)	10.0447(3)	15.2140(5)	44.675(1)
c/Å	6.1895(2)	9.9978(5)	11.3905(4)	13.9494(4)	12.1963(4)	14.6413(3)
α/°				98.995(2)		
β/°		92.039(3)	106.141(2)	93.178(2)		93.004(2)
γ/°				101.633(2)		
U/Å^3	623.63(3)	721.40(5)	2446.5(1)	1108.43(6)	1370.04(7)	8028.1(3)
Z	4	4	4	1	4	24
D_c/g cm^{-3}	1.817	1.820	1.563	1.602	1.512	1.548
μ(Mo-Kα)/mm^{-1}	3.403	2.956	1.774	1.950	1.590	1.628
Data collected	8260	9313	10124	10456	11519	49758
Unique data (R_{int})	788 (0.0320)	1658 (0.052)	3407 (0.0275)	6753 (0.0351)	3039 (0.0293)	22290 (0.0554)
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0186, 0.0418	0.0335, 0.0549	0.0567, 0.1618	0.0378, 0.0897	0.0256, 0.0519	0.0560, 0.1200
(all data)	0.0212, 0.0425	0.0529, 0.0594	0.0753, 0.1836	0.0611, 0.0997	0.0324, 0.0542	0.0884, 0.1363

dimensions (from 1-D to 3D). In addition, new and unusual forms of interpenetration have been displayed, and it is important to the examination of networks in crystal structures that we understand not only the topology of the networks which interpenetrate, but also the topology of the interpenetration itself.

Experimental

Preparations

Cu(dca)(MeCN) 1. Solutions of Cu(MeCN)$_4$(ClO$_4$) (240 mg, 0.73 mmol) in acetonitrile (12 cm^3) and [PPN][dca] (679 mg, 1.12 mmol) in acetone–acetonitrile (1 : 1, 18 cm^3) were mixed, resulting in precipitation of colourless crystals of **1** over 24 h (67 mg, 0.40 mmol, 55%) (Found: C, 24.88; H, 1.29; N, 31.70%. $C_2CuN_3{\cdot}0.6C_2H_3N$ requires C, 24.92; H, 1.18; N, 32.70%); $\tilde{\nu}_{max}$/cm^{-1} (2300–2000) 2290s, 2236vs and 2155 (sh) (KBr). The analysis and powder X-ray diffraction patterns indicated probable decomposition due to loss of acetonitrile.

Cu(dca)(Me$_4$pyz)$_{1/2}$ 2. Warm solutions of Cu(MeCN)$_4$(ClO$_4$) (120 mg, 0.37 mmol) in acetonitrile (12 cm^3), Me$_4$pyz (25 mg, 0.18 mmol) in acetone (9 cm^3), and [PPN][dca] (340 mg, 0.56 mmol) in acetone (9 cm^3) were mixed. Colourless crystals of compound **1** were filtered off after 3 h, and yellow crystals of **2** formed over 24 h (6 mg, 0.03 mmol, 8%) (Found: C, 36.44; H, 3.21; N, 28.27%. $C_6H_6CuN_4$ requires C, 36.45; H, 3.07; N, 28.35%); $\tilde{\nu}_{max}$/cm^{-1} (2320–2000) 2312s, 2254s, 2206s and 2182vs (KBr). The powder X-ray diffraction pattern was consistent with the single crystal structure.

Cu$_2$(dca)$_2$(bipy)(MeCN)$_2$·0.5bipy 3. Hot solutions of Cu(MeCN)$_4$(ClO$_4$) (40 mg, 0.12 mmol) in acetonitrile (2 cm^3), bipy (19 mg, 0.12 mmol) in acetonitrile (10 cm^3), and [PPN][dca] (74 mg, 0.12 mmol) in acetonitrile (10 cm^3) were mixed, resulting in precipitation of yellow-orange dichromic crystals of **3** over 24 h (16 mg, 0.028 mmol, 47%) (Found: C, 47.35; H, 3.25; N, 27.30%. $C_{23}H_{18}Cu_2N_{11}$ requires C, 47.99; H, 3.16; N, 26.77%); $\tilde{\nu}_{max}$/cm^{-1} (2300–2000) 2291 (sh), 2261s, 2210 (sh), 2172vs and 2155vs (KBr). The powder X-ray diffraction pattern indicated the bulk was consistent with the single crystal structure.

Cu$_4$(dca)$_4$(bipy)$_3$(MeCN)$_2$ 4. If the reaction for compound **3** is left undisturbed for between one and three days the yellow-orange crystals of **3** are replaced by dark red crystals of **4** (23 mg, 0.022 mmol, 73%) (Found: C, 47.13; H, 2.70; N, 26.51%. $C_{21}H_{15}Cu_2N_{10}$ requires C, 47.18; H, 2.83; N, 26.21%); $\tilde{\nu}_{max}$/cm^{-1} (2300–2000) 2283s, 2233m and 2175vs (KBr). The powder X-ray diffraction pattern indicated the bulk was consistent with the single crystal structure.

α-Cu(dca)(bpe) 5 and β-Cu(dca)(bpe) 6. Hot solutions of Cu(MeCN)$_4$(ClO$_4$) (40 mg, 0.12 mmol) in acetonitrile (2 cm^3), bpe (44 mg, 0.24 mmol) in acetonitrile (10 cm^3), and [PPN][dca] (148 mg, 0.24 mmol) in acetonitrile (10 cm^3) were mixed, resulting in instant precipitation of an amorphous yellow powder (18 mg) (Found: C, 43.23; H, 2.75; Cu, 25.8; N, 23.81%); $\tilde{\nu}_{max}$/cm^{-1} (2300–2000) 2291s, 2240s and 2177vs (KBr).

This yellow precipitate was filtered off, and formation of a mixture of orange (**5**) and dark red (**6**) crystals followed (6 mg, 0.019 mmol, 16%). These products were separated manually for characterisation: **5** (Found: C, 54.06; H, 3.37; N, 22.37%. $C_{14}H_{10}CuN_5$ requires C, 53.92; H, 3.24; N, 22.46%). $\tilde{\nu}_{max}$/cm^{-1} (2300–2000) 2258s, 2214w and 2150vs (KBr); **6** (Found: C, 54.16; H, 3.44; N, 22.62%). $\tilde{\nu}_{max}$/cm^{-1} (2300–2000) 2276s, 2227w and 2171vs (KBr). The powder X-ray diffraction patterns of both samples indicated the bulk was consistent with the single crystal structures.

Crystallography

Crystal data and details of the structure determinations are presented in Table 1. Data were collected at 123(2) K on a Nonius KappaCCD diffractometer. Absorption corrections (face-indexed) were applied only to the data for compounds **1** and **2**, and the structures were refined against F^2. The non-centrosymmetric structures **5** and **6** were refined as racemic twins; satisfactory solutions could not be obtained with centrosymmetric space groups. The guest bipy molecules in **3** were constrained to a sensible geometry, and refined isotropically. All other non-hydrogen atoms in the structures were made anisotropic. All hydrogen atoms were assigned to calculated positions except those on the guest bipy molecules in **3**, which were neither detected nor assigned.

CCDC reference number 186/2023.

See http://www.rsc.org/suppdata/dt/b0/b003527k/ for crystallographic files in .cif format.

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