FULL PAPER

Interdigitation, Interpenetration and Intercalation in Layered Cuprous Tricyanomethanide Derivatives

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Abstract: Reaction of Cu^I, tricyanomethanide (tcm⁻, $C(CN)_3^-$) and L = either hexamethylenetetramine (hmt), 4,4′-bipyridine (bipy) or 1,2-bis(4-pyridyl)ethene (bpe) gives crystals of [Cu(tcm)(hmt)] (**1**), [Cu(tcm)(bipy)] (**2**) and [Cu(tcm)(bpe)] · 0.25 bpe · 0.5 MeCN (**3**), respectively. Crystal structure analysis shows **1 – 3** all contain closely related puckered (4,4) sheets composed of tetrahedral Cu^I ions bridged by 2-connecting tcm⁻ and L. The crystal packing, however, varies markedly with L. In **1** the sheets interdigitate in pairs. In **2** the sheets participate in parallel interpenetration in pairs. In **3** guest bpe and MeCN molecules are intercalated in channels formed by the stacking of the sheets.

Introduction

Coordination polymer frameworks are much studied at present.[1] A major reason for this interest is the promise of being able to generate by deliberate design new materials with useful tailor-made properties but coordination polymers are important also for the less utilitarian reason that they constitute a unique and interesting branch of fundamental structural chemistry.

With specific regard to two-dimensional networks, three distinctly different strategies can be discerned whereby sheets containing significant holes contrive to occupy space efficiently, namely, interdigitation of adjacent sheets,[2] interpenetration of the sheets,[3] and intercalation of guests;[4] examples of each of these strategies are found in the closely related sheet structures reported in this paper. The two major classes of interpenetration seen with sheet structures are *parallel interpenetration* in which each sheet is intimately entangled with a finite number of others (often two but occasionally more) whose mean planes are parallel, and *inclined interpenetration* in which the mean planes of the sheets are not all parallel and each sheet is penetrated by an infinite number of inclined ones.[3] Intercalation of ordered guest molecules or counterions into sheet structures can be broadly classed as *through-sheet*, *between-sheet* and *within-sheet intercalation*.

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The results presented below arose out of our ongoing interest in coordination polymers containing the ligand tcm⁻ (tricyanomethanide, $C(CN)_3^-$, Scheme 1). The structures of the binary compounds [M(tcm)₂], in which M is one of a wide
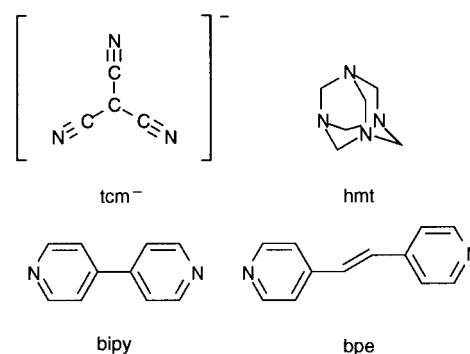
Scheme 1. Ligands used in this work.

range of divalent octahedral metal ions and tcm⁻ plays a 3-connecting role, contain two independent and interpenetrating three-dimensional (3D) nets with the topology of the rutile prototype.[5] The infinite 3D framework in [Cd(tcm)(B(OMe)₄)] · *x* MeOH is chiral and is constructed from 3-connecting tcm⁻ ions and bridging, chelating $B(OMe)_4^-$ ions.[6] [Cd(tcm)(hmt)(H₂O)](tcm), hmt = hexamethylenetetramine, has a rutile-related network structure in which both the tcm⁻ and the hmt moieties are 3-connecting; uncoordinated tcm⁻ ions which hydrogen bond to water ligands are also present.[7] The tcm⁻ ligand, often in the company of monodentate nitrogen-donor co-ligands, forms a number of other polymeric compounds with metal ions.[8]

[Ag(tcm)] consists of corrugated hexagonal (6,3) sheets whose 3-connecting nodes are provided by both tcm⁻ and

three-coordinate silver; pairs of sheets of this type interpenetrate in the parallel mode.[9, 10] The closely related structure of [Ag(tcm)(MeCN)] contains pairs of interpenetrating sheets very similar to those in the unsolvated parent but now each silver is four-coordinate carrying a monodentate MeCN ligand which increases the separation between adjacent composite sheets.[9] Analogous Ag(tcm) double layers are bridged by phenazine (phz) ligands in [Ag(tcm)(phz)$_{1/2}$] to give two interpenetrating 3D nets.[9] Two interpenetrating 3D networks are also seen in the structures of [Ag(tcm)(L)] in which L = pyrazine, 1,4-diazobicyclo[2.2.2]octane, or 4,4'-bipyridine (bipy),[9] but in these cases the Ag(tcm) (6,3) sheets are internally planar in contrast to the corrugated ones in the parent [Ag(tcm)] and its MeCN and phz derivatives. The L ligands connect each planar Ag(tcm) sheet to two others, one on each side, the Ag centres acquiring thereby a trigonal-bipyramidal coordination geometry. The structures of [Ag(tcm)(Me$_4$pyz)$_{1/2}$] (Me$_4$pyz = tetramethylpyrazine) and [Ag(tcm)(bpe)] (bpe = 1,2-bis(4-pyridyl)ethene) are different again.[9]

This rich structural variety shown by [Ag(tcm)] derivatives prompted us to investigate analogous [Cu^I(tcm)] systems with the very different outcomes described below.

Results and Discussion

Reaction of hexamethylenetetramine (hmt) with Cu^I and tcm$^-$ in acetonitrile gave crystals of [Cu(tcm)(hmt)] (**1**), whose structure was determined by single-crystal X-ray diffraction (see Tables 1 and 2 and Figures 1 and 2). The

Table 1. Selected crystallographic and data collection parameters for compounds **1**–**3**.

	[Cu(tcm)(hmt)]	[Cu(tcm)(bipy)]	[Cu(tcm)(bpe)]·0.25 bpe·0.5 MeCN
	(**1**)	(**2**)	(**3**)
molecular formula	CuC$_{10}$N$_7$H$_{12}$	CuC$_{14}$N$_5$H$_8$	CuC$_{20}$N$_6$H$_{14}$
M	293.83	309.81	401.94
crystal system	orthorhombic	orthorhombic	monoclinic
space group	$Cmcm$ (no. 63)	$Pcab$ (no. 61)	$P2_1/c$ (no. 14)
a [Å]	8.027(2)	7.651(2)	7.882(2)
b [Å]	23.230(5)	17.995(3)	25.465(5)
c [Å]	6.188(2)	20.450(5)	18.713(6)
β [°]	–	–	96.63(3)
U [Å^3]	1153.9	2815.5	3730.6
Z	4	8	8
T [K]	295(1)	295(1)	295(1)
ρ_{calcd}, ρ_{obs} [g cm^{-3}]	1.69, 1.67(2)	1.46, 1.46(1)	1.43, 1.45(1)
μ [cm^{-1}]	18.60	15.23	11.62
$2\theta_{max}$ [°]	60	52	50
data collected	1339	4078	9143
unique data (R_{int})	972 (0.0123)	2759 (0.0353)	6923 (0.0181)
observed data	596 [$I3\sigma(I)$]	488 [$I3\sigma(I)$]	4032 [$I2\sigma(I)$]
transmission factors	0.8707 – 0.9738	0.8774 – 0.9786	0.8173 – 0.9350
number of parameters	68	88	510
R[a]	0.0376	0.0819	0.0629
R_w[b]	0.0344	0.0677	0.0534
weighting scheme (k, g)[c]	1.1949, 0.0002	3.201, 0.001	1.9443, 0.0002
goodness of fit	1.259	1.918	1.463
$\Delta\rho_{max}$ [e Å^{-3}]	0.37	0.65	0.60

[a] $R = \Sigma |\Delta F|/\Sigma |F_o|$. [b] $R_w = \Sigma w^{1/2} |\Delta F|/\Sigma w^{1/2} |F_o|$. [c] $w = k[\sigma^2(F_o) + g |F_o|^2]^{-1}$.
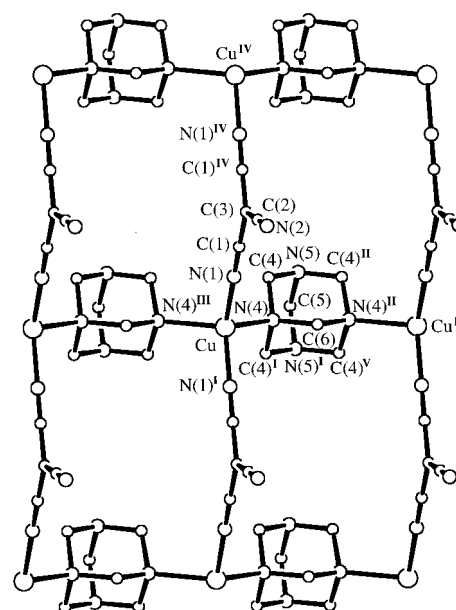

Figure 1. Atom numbering and (4,4) sheet structure of **1**.

Table 2. Selected interatomic distances [Å] and angles [°] for **1**.[a]

Cu–N(4)	2.223(3)	Cu–N(1)	1.929(4)
Cu···Cu^{IV}	8.027	Cu···Cu^{II}	6.188
N(4)-Cu-N(1)	103.35(7)	N(4)-Cu-N(1)^I	103.35(7)
N(4)-Cu-N(4)^{III}	114.02(9)	N(1)-Cu-N(4)^{III}	103.35(7)
N(1)-Cu-N(1)^I	129.8(2)	Cu-N(1)-C(1)	179.9(4)

[a] Symmetry transformations: (I): $-x, y, z$; (II): $x, y, -0.5 - z$; (III): $x, y, 0.5 - z$; (IV): $1 - x, y, z$.

copper centres, all of which are equivalent with a distorted tetrahedral coordination geometry, provide the 4-connecting nodes in (4,4) rectangular grid sheets (Figures 1 and 2). The copper atoms within a sheet are all coplanar. The sides of the rectangles of the grid lying parallel with the a axis are provided by 2-connecting tcm$^-$ bridges and the sides parallel with the c axis are provided by hmt bridges which are also 2-connecting. Both ligands have a non-linear bridging geometry and all the hmt ligands are located on one side of the plane of the copper centres and all the tcm$^-$ units on the other. The structure provides a very nice example of interdigitation. The sheets occur in discrete pairs in which the rod-like
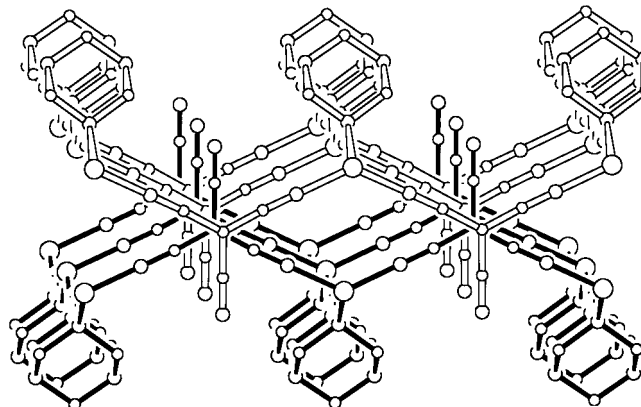

Figure 2. Interdigitation within a pair of puckered (4,4) sheets in **1**.

uncoordinated nitrile groups of one penetrate the rectangular windows of the partner, as can be clearly seen in Figure 2. The interdigitating tcm⁻ units make very close contact; adjacent trigonal carbon centres are separated by only 3.10 Å. The tcm···tcm separation within a given sheet is dictated by the Cu-hmt-Cu separation (6.19 Å) which coincidentally allows this very snug interdigitation. It appears that the interdigitation can only be accomplished by slightly stretching the Cu−N(hmt) bonds which are somewhat longer (2.223(3) Å) than those seen in [(Cu(CN))₃(hmt)₂] (2.104(3) and 2.172(3) Å).[11]

Reaction of Cu^I, tcm⁻ and 4,4′-bipyridine (bipy) in acetonitrile gave crystals of [Cu(tcm)(bipy)] (**2**), whose structure was determined by single-crystal X-ray diffraction (see Tables 1 and 3 and Figures 3 and 4). The structure consists of corrugated (4,4) sheets in which distorted tetrahedral copper centres provide the 4-connecting nodes and tcm⁻ and bipy both act as 2-connectors. In contrast to the [Cu(tcm)(hmt)]

those in the two adjacent chains are on the opposite side. The corrugated nature of the sheets allows them to interpenetrate in pairs in the parallel mode[3] (Figures 3 and 4). Each Cu₄(tcm)₂(bipy)₂ window is penetrated by one Cu-bipy-Cu rod of the other sheet. All bipy units are equivalent but the pyridyl components of each bipy are of two types, one of which appears in face-to-face columns running in the *a* direction clearly visible in both Figures 3 and 4 (centroid–centroid separation = a/2 = 3.83 Å, probably too large to suggest any significant π–π interaction). The second type of pyridine ring is rotated around the central C−C bond of the bipy by 27.5° relative to the first. Rod-like uncoordinated nitrile groups project like bristles from both sides of the composite paired-up sheets and interdigitate with adjoining composites as can be clearly seen in Figure 4. The interdigitating tcm⁻ bristles, however, are further apart than those in **1** (closest contact is C1···C2 = 3.65 Å). The terminal N of the bristles is located 2.52 Å from a H atom of a bipy in the adjacent composite layer, possibly indicative of what could be described as a weak C−H···N hydrogen bond.[12]
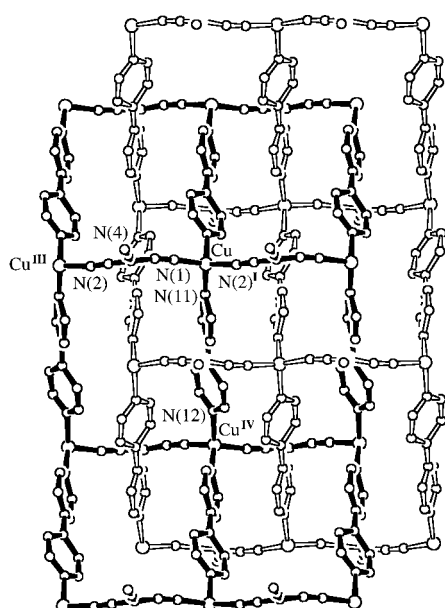

Figure 3. Two interpenetrating (4,4) sheets and selected atom numbering for **2**.

Table 3. Selected interatomic distances [Å] and angles [°] for **2**.[a]

Cu−N(1)	1.95(2)	Cu^{III}−N(2)	1.97(3)
Cu−N(11)	1.97(3)	Cu^{IV}−N(12)	2.09(3)
Cu···Cu^{III}	7.651(5)	Cu···Cu^{IV}	11.203(7)
N(1)-Cu-N(11)	111(1)	N(1)-Cu-N(12)^{II}	105(1)
N(1)-Cu-N(2)^I	115(1)	N(11)-Cu-N(2)^I	110(1)
N(11)-Cu-N(12)^{II}	105(1)	N(2)^I-Cu-N(12)^{II}	111(1)
Cu-N(1)-C(1)	176(2)	Cu^{III}-N(2)-C(2)	172(3)

[a] Symmetry transformations: (I): 1 + x, y, z; (II): x, y − 0.5, 0.5 − z; (III): x − 1, y, z; (IV): x, 0.5 + y, 0.5 − z.

example above the copper atoms within a sheet are not all coplanar; rather, half fall in one plane, half in a separate parallel plane. Within a single sheet infinite Cu/tcm⁻ chains, in which the copper atoms are colinear, run in the *a* direction. These Cu/tcm⁻ chains are arranged such that the uncoordinated nitrile groups in one are all on one side of the sheet and
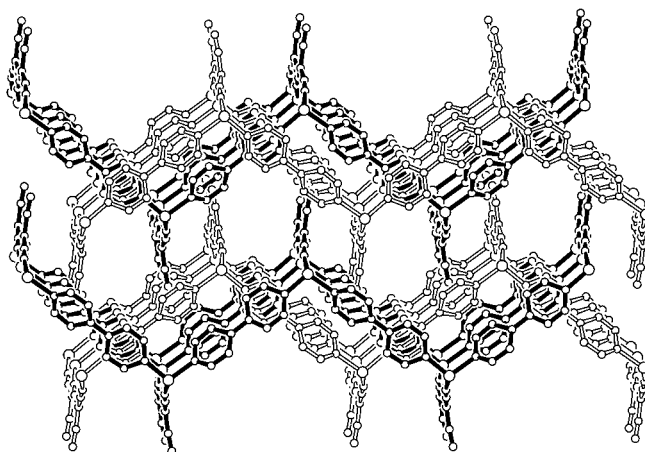

Figure 4. Interdigitation of layers of doubly interpenetrating puckered sheets in **2**.

Reaction of Cu^I, tcm⁻ and 1,2-bis(4-pyridyl)ethene (bpe) gave yellow crystals of [Cu(tcm)(bpe)] · 0.25 bpe · 0.5 MeCN (**3**), whose structure was determined by single-crystal X-ray diffraction (see Tables 1 and 4 and Figures 5 – 8). The structure consists of corrugated Cu(tcm)(bpe) sheets with a (4,4) topology and a geometry very similar to those seen in [Cu(tcm)(bipy)] above. Cu/tcm⁻ chains in which the metals are colinear run in the *a* direction. Zig-zag Cu/bpe chains run in the *c* direction. The metal again has a distorted tetrahedral coordination geometry. Uncoordinated nitriles of tcm⁻ bristle out in opposite directions from the two sides of the sheet, much as in [Cu(tcm)(bipy)] (Figure 6). In [Cu(tcm)(bpe)] · 0.25 bpe · 0.5 MeCN, however, there is no interpenetration; instead, through-sheet intercalation of guest molecules occurs. Channels of roughly square cross-section running in the *b* direction formed by the stacking of the sheets are occupied by uncoordinated bpe molecules and twice as many acetonitrile guests which alternate along the channels in the order, -bpe-MeCN-NCMe-bpe-MeCN-NCMe-bpe- (Figures 7 and 8). As
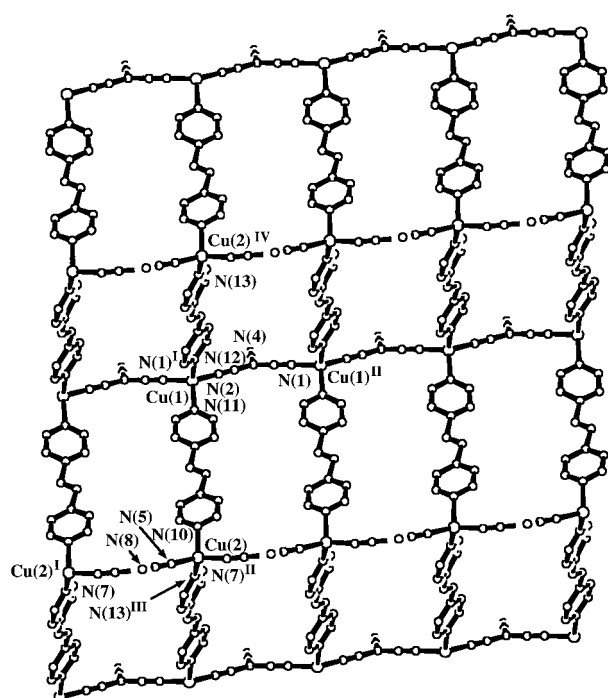
Figure 5. A Cu(tcm)(bpe) sheet with selected atom numbering in **3**.

Table 4. Selected interatomic distances [Å] and angles [°] for **3**.[a]

Cu(1)−N(2)	1.950(4)	Cu(1)−N(11)	2.080(5)
Cu(1)−N(12)	2.114(4)	Cu(1)^{II}−N(1)	1.952(4)
Cu(2)−N(5)	1.948(4)	Cu(2)−N(10)	2.106(4)
Cu(2)^{I}−N(7)	1.942(4)	Cu(2)^{III}−N(13)	2.060(4)
Cu(1)···Cu(1)^{II}	7.882(2)	Cu(2)···Cu(2)^{I}	7.882(2)
Cu(2)···Cu(2)^{III}	18.713(6)		
N(2)-Cu(1)-N(12)	103.7(2)	N(2)-Cu(1)-N(11)	115.3(2)
N(2)-Cu(1)-N(1)^{I}	120.9(2)	N(11)-Cu(1)-N(12)	96.9(2)
N(11)-Cu(1)-N(1)^{I}	104.0(2)	N(5)-Cu(2)-N(10)	110.4(2)
N(5)-Cu(2)-N(7)^{II}	121.7(2)	N(5)-Cu(2)-N(13)^{III}	105.2(2)
N(10)-Cu(2)-N(7)^{II}	104.7(2)	N(10)-Cu(2)-N(13)^{III}	99.6(2)
N(7)^{II}-Cu(2)-N(13)^{III}	113.1(2)		

[a] Symmetry transformations: (I): $1+x, y, z$; (II): $x-1, y, z$; (III): $x, y, z-1$.
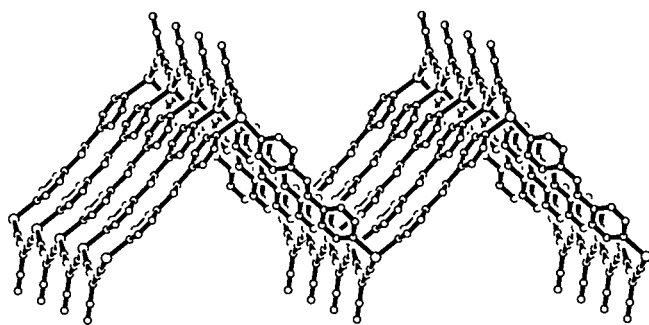

Figure 6. A side-on view of the puckered (4,4) sheet in **3**.

will be apparent on inspection of Figure 8 (left), two types of framework bpe ligands are present, differing in the orientation of their pyridine rings. One type (type A) is seen in the close vicinity of the channel bpe ligands which are encircled by two equivalent rings of composition Cu₄(tcm)₂(bpe)₂, one from each of two separate sheets (Figure 8 left). The second
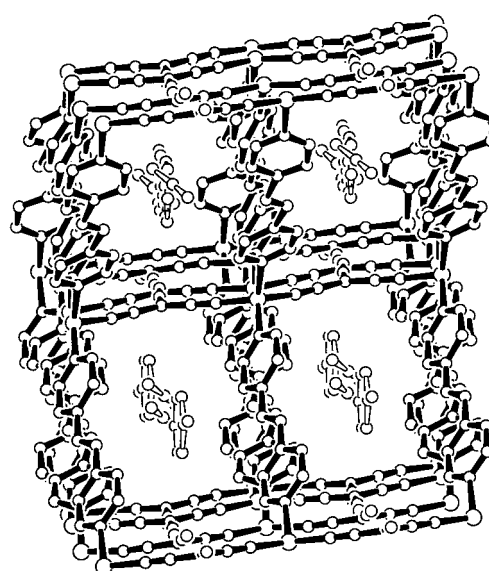

Figure 7. Intercalation of guest bpe and MeCN molecules in the rectangular channels of **3** created by stacking of the Cu(tcm)(bpe) sheets.
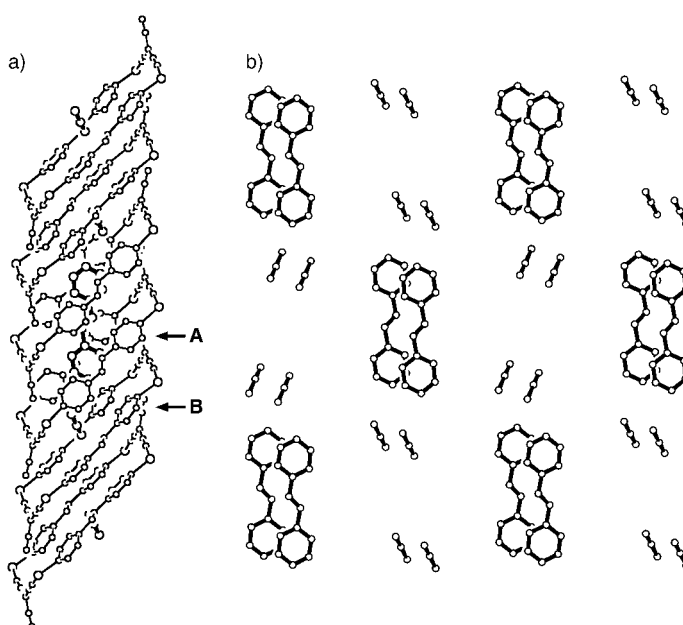

Figure 8. Left) A fraction of a single channel in **3** showing Cu₄(tcm)₂(bpe)₂ rings from six separate sheets encircling one uncoordinated bpe (centrally placed in this view) and four acetonitrile guest molecules. The two types of sheet bpe ligand (A and B) are also shown. Right) The bpe and MeCN guests in eight channels viewed from the same aspect as in a).

type of framework bpe ligand (type B) is involved in encirclement of the two MeCN molecules. Apparently the orientations of the pyridine rings of the framework bpe ligands adjust themselves to the requirements of the particular intercalated species (bpe or MeCN) with which they make close contact. No outstanding, obviously structure-determining, intermolecular contacts are apparent, although some specific interactions, considered below, can be identified which may have significance with regard to the structure adopted. All framework bpe ligands, whether type A or type B, make moderately close contact with two others belonging to adjacent sheets, one type A and the other type B. The

closest non-hydrogen type A to type A contact is a C···C separation of 3.32 Å, indicating significant $\pi-\pi$ interaction (offset). Less pronounced interaction is evident between type B ligands, the closest C···C separation being 3.53 Å. There are no non-hydrogen contacts between type A and type B ligands of any significance. There is a suggestion of a weak C–H···π hydrogen bond[13] between a pyridyl hydrogen of one of the framework type A bpe ligands and the C=C π system in the guest bpe molecule (H···X = 2.61 Å, H···C = 2.64, 2.73 Å, C–H···X = 148°, where X is the midpoint of the C=C bond).

The compounds described here have much in common; all are Cu(tcm) derivatives in which the metal is tetrahedral and all contain puckered (4,4) rectangular grid sheets in which both tcm⁻ and the co-ligands act as 2-connecting bridges. Despite this close relationship the structures adopted differ markedly, representing each of the three main ways in which porous sheet arrangements achieve packing efficiency—**1** interdigitates, **2** interpenetrates and **3** intercalates. It is clear that the preference for one packing motif over another is determined in a complex and subtle manner by the summation of a very large number of weak interactions. Although we are unable to propose definitive reasons as to why each compound adopts a different strategy to minimise its energy the following simple observations can be made. In **1**, the shortness and bulkiness of the hmt bridge means that the rectangular windows in the individual sheets are too small and sterically cramped to allow interpenetration. In **2** and **3**, the co-ligands, bipy and bpe, being considerably longer and sterically less bulky, make penetration by other nets or by guest molecules feasible. Some indication of the packing efficiency of a structure is afforded by the volume per non-hydrogen atom, which is 16.0 Å³ for **1**, 17.6 Å³ for **2** and 17.3 Å³ for **3**, relatively low figures as coordination polymers go, indicating relatively efficient packing. If one takes the dimensions of the puckered sheets in the bpe structure and calculates the theoretical packing efficiency for the hypothetical arrangement with the same parallel interpenetrating structure as is observed for [Cu(tcm)(bipy)] the calculated volume per non-hydrogen atom is about 22.3 Å³. Clearly for bpe the observed through-sheet intercalated arrangement is a much more efficient alternative. A number of moderately close contacts between the bpe guests and the Cu(tcm)(bpe) sheets suggest that the channels provide a reasonably snug fit for the guests, as is supported by the relatively small volume per non-hydrogen atom. Replacement of bpe with bipy would result in a reduction of the channel dimensions, possibly by an amount too great to allow intercalation of guest bipy molecules.

The results presented here serve to emphasise the magnitude of the problem involved in attempting to determine by computation the structure of a coordination polymer simply on the basis of the components present in the reaction mixture from which it grows. In the general coordination polymer case, in addition to the subtle balances between many weak forces of attraction and repulsion, of the sort responsible for the variety of structural outcomes seen in the particular systems reported here, there are additional areas of major unpredictability such as the coordination geometries of both metal and

ligands: using again the particular systems considered here to illustrate the general point, tcm⁻ in the above Cu compounds acts uniformly as a 2-connector, yet in the Ag analogues it acts as a 3-connector.

Experimental Section

General procedure: Hmt, bipy, bpe, Me₄NBr and all non-aqueous solvents were purchased from commercial sources and used as supplied. [Me₄N][tcm] was synthesised by aqueous metathesis of Me₄NBr and K[tcm].[5b, 14]

Synthesis of 1: Reaction of [Cu(MeCN)₄](ClO₄) (353 mg, 1.1 mmol) in acetonitrile (10 mL), [Me₄N][tcm] (189 mg, 1.2 mmol) in acetonitrile (50 mL) and hexamethylenetetramine (329 mg, 2.3 mmol) in acetonitrile (25 mL) gave fine colourless needles of **1** after three days. Yield: 99 mg (31 %); IR (KBr disk): $\tilde{\nu} = 500$, 516, 547, 617, 660, 680, 698, 775, 795, 823, 926, 998, 1017, 1029, 1050, 1225, 1232, 1240, 1263, 1350, 1362, 1382, 1442, 1479, 1484, 2180, 2470, 2860, 2940, 3430 (br) cm⁻¹; anal. calcd for CuC₁₀N₇H₁₂: Cu 21.62, C 40.87, N 33.38, H 4.12; found: Cu 21.03, C 41.07, N 33.25, H 3.93. X-ray powder diffraction of the bulk sample indicated the crystal structure reported here is consistent with the bulk of the product obtained.

Synthesis of 2: Reaction of [Cu(MeCN)₄](ClO₄) (32 mg, 0.098 mmol) in acetonitrile (1 mL), [Me₄N][tcm] (18 mg, 0.11 mmol) in acetonitrile (10 mL) and 4,4′-bipyridine (15 mg, 0.096 mmol) in acetonitrile (5 mL) gave fine yellow needles of **2**. Yield: 16 mg (54 %); IR (weak, KBr disk): $\tilde{\nu} = 552$, 603, 626, 729, 805, 1065, 1218, 1250, 1320, 1365, 1410, 1488, 1536, 1602, 2200, 3445 (br) cm⁻¹; anal. calcd for CuC₁₄N₅H₈: C 54.27, N 22.61, H 2.61; found: C 53.28, N 22.30, H 2.44. The crystal structure was performed on a crystal obtained from a more dilute (ca. one-half the concentration of Cu) reaction to that detailed above which contained a five-fold excess of bipy. Crystallisation was much slower, and gave low yields of larger crystals suitable for crystallography. Several different single crystals from the lower concentration reaction gave identical cell parameters. Although the bulk product obtained from the concentrated reaction looked identical in morphology and colour to that obtained from the less concentrated reaction (except the crystals obtained thereby were larger), elemental and powder diffraction analysis indicates possible formation of a second, as yet unidentified product.

Synthesis of 3: Reaction of [Cu(MeCN)₄](ClO₄) (32 mg, 0.098 mmol) in acetonitrile (1 mL), [Me₄N][tcm] (20 mg, 0.12 mmol) in acetonitrile (30 mL) and 1,4-bis(4-pyridyl)ethene (89 mg, 0.49 mmol) in acetonitrile (15 mL) gave a yellow solution which produced orange crystals of **3** after four days. Yield: 20 mg (51 %); IR (KBr disk): $\tilde{\nu} = 550$, 616, 823, 975, 1010, 1066, 1219, 1256, 1297, 1422, 1500, 1542, 1553, 1603, 2180, 2910, 2160, 2230, 3410 (br) cm⁻¹; anal. calcd for CuC₂₀N₆H₁₄·0.7H₂O: Cu 15.29, C 57.80, N 20.23, H 3.98; found: Cu 15.37, C 58.20, N 19.94, H 3.18. X-ray powder diffraction of the bulk sample indicated the crystal structure reported here is consistent with the bulk of the product obtained.

Crystallography: Crystal data and details of the structure determinations are presented in Table 1. A clear colourless crystal (0.014 × 0.072 × 0.21 mm) of **1** and a yellow needle (0.014 × 0.086 × 0.14 mm) of **2** were mounted on glass fibres, while the orange crystal (0.058 × 0.17 × 0.31 mm) of **3** was sensitive to solvent loss and sealed with mother liquor in a Lindemann glass capillary. The intensity data were collected using the ω:2θ scan technique on an Enraf-Nonius CAD-4F diffractometer fitted with Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) and a graphite monochromator. Accurate values for the unit cell parameters and crystal orientation were obtained by a least-squares procedure from the angular settings of 25 automatically centred reflections. During data collection three reflections were used as orientation controls and measured every 150 reflections. Similarly, three further reflections were used as intensity controls and measured every 10 000 s. Significant crystal decay was observed only for **3**, and the data was adjusted accordingly.

Corrections for Lorentz, polarisation and absorption effects were applied to the data. The structure of **1** was solved from the Patterson functions (SHELXS-86).[15] All hydrogens were found in the subsequent difference maps, assigned to calculated positions and refined with a common isotropic

thermal parameter. Anisotropic thermal parameters were applied to all non-hydrogen atoms. For **2** the structure was solved using direct methods (SHELXS-86). All hydrogen atoms were assigned to calculated positions and refined with a common isotropic thermal parameter. Anisotropic thermal parameters were applied to only the copper atoms. In the structure of **3** the positions of all non-hydrogen atoms except those of the acetonitrile guests were determined using direct methods (SHELXS-86). The atoms of the acetonitrile ligand and all hydrogen atoms were found in the subsequent difference maps, and the hydrogens were assigned to calculated positions. All pyridyl hydrogens of the bpe ligands within the sheets were assigned a common isotropic thermal parameter, as were all ethene bpe hydrogen atoms within the sheets, and all pyridyl hydrogens of the guest bpe molecules. The isotropic thermal parameters of the acetonitrile hydrogens were fixed at 0.15. Anisotropic thermal parameters were applied to all non-hydrogen atoms.

Refinements for all structures were achieved using the SHELX-76 system.[16] Weighting schemes of the form $w = k[\sigma^2(F_o) + g |F_o|^2]^{-1}$ were used with the parameters k and g being redetermined at the end of each cycle. Anisotropic extinction parameters x were also included in the refinements so that F_c was modified according to $F_c(\mathrm{corr}) = F_c(1 - xF_c^2/\sin\theta)$. They refined to values of 0.07(3), −0.018(9), and −0.001(4) × 10⁶ for **1**, **2** and **3**, respectively. The parameters used for the scattering curves of C, H, and N were those incorporated into the SHELX-76 system. Coefficients for the scattering curves for all other elements present were those for their atomic forms taken from *International Tables for X-ray Crystallography Vol. IV*;[17] corrections were made for anomalous dispersion.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-118844 (**1**), CCDC-118845 (**2**) and CCDC-118846 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

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