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Self-assembly of copper(I) complexes into three-dimensional co-ordination polymers with channel networks by hydrogen bonding or by tridentate ligands

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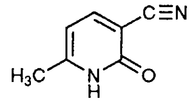
Reaction of the appropriate copper(I) salt with 3-cyano-6-methylpyridin-2(1*H*)-one (Hcmp) gave three polymeric co-ordination compounds, $[Cu(cmp)(Hcmp)_3]\cdot C_5H_{12}$ **1**, $[Cu_2(Hcmp)_4(Me_2CO)_2][BF_4]_2$ **2** and $[Cu_5(cmp)_4]ClO_4$ **3**, the structures of which have been determined by X-ray crystallography. Complex **1** contains a three-dimensional supramolecular framework of tetrahedral CuN_4 centres linked by intermolecular hydrogen bonds through the pyridone N and O atoms. The open square microchannels created enclathrate *n*-pentane as the guest molecule. Complex **2** contains a dimeric unit weakly bound by the bridging acetone oxygen atoms. Each Hcmp moiety in the dimer is hydrogen-bonded pairwise to one adjacent Hcmp molecule belonging to the other dimer giving a one-dimensional array of copper atoms. The unique structural feature of complex **3** is that it does not involve hydrogen bonding as in **1** or **2**, instead each cmp monoanion employs all its three functional groups bridging three copper atoms forming a supramolecular channel architecture containing a Cu_4 cluster. The results are discussed in terms of designing new inorganic solids by the self-assembly of copper(I) complexes.

Hydrogen bonding has been noted as a most powerful organizing force in the self-assembly of organic molecules into one-, two- or three-dimensional hydrogen-bonded architectures.[1–6] In respect of the construction of the corresponding co-ordination supramolecules the synthetic strategy relies primarily upon the use of a bridging ligand to link the metal cations,[7–11] with less attention paid to the exploitation of non-covalent intermolecular interactions such as hydrogen bonding.[12,13] Among several notable examples of supramolecular structures the one with three-dimensional channel networks has received considerable interest in both organic and inorganic chemistry since it shows great promise for a number of applications such as selective enclathration, microporosity and catalytic activity.[5–7] Wuest and co-workers[6] have demonstrated that self-association of di- and tetra-pyridone through hydrogen bonding can produce two- and three-dimensional organic diamondoid networks with large internal rectangular channels similar to the behaviour of zeolites. In order to build the corresponding metallosupramolecular systems the ligand is required to have multifunctional groups. Since 3-cyano-6-methylpyridin-2(1*H*)-one (Hcmp) possesses both a co-ordination group (CN) and a hydrogen-bonding site (NH $\cdots$ O) in the solid state, the speculation that three-dimensional networks might be formed from this basic building block has prompted us to prepare and characterize members of this new class of materials.

In pursuit of controlled synthesis of new solids from association of mono- or di-nuclear units, we have reported a number of one-, two- and three-dimensional polymeric metal complexes connected through hydrogen bonding,[14] π–π interactions[15] or S $\cdots$ S contacts[16] as well as co-ordination bonds.[14,17] Here we report a new type of self-assembly of copper(I) complexes of Hcmp by hydrogen bonds or through bridging of the tridentate ligands.

Experimental

Preparations were performed using Schlenk techniques. All solvents were dried and distilled by standard methods before use. The salts $[Cu(MeCN)_4]PF_6$ and $[Cu(MeCN)_4]BF_4$ were synthesized according to literature procedures.[18] Reagent grade 3-cyano-6-methylpyridin-2(1*H*)-one was obtained from Aldrich Chemicals. All other chemicals were purchased from Wako Pure Chemical Co., Japan, and used without further purification. Infrared spectra were recorded as KBr discs on a JASCO 8000 FT-IR spectrometer. **CAUTION**: One of the following preparations uses $Cu(ClO_4)_2\cdot 6H_2O$ which is potentially explosive.



Hcmp

Syntheses

$[Cu(cmp)(Hcmp)_3]\cdot C_5H_{12}$ 1. The salt $[Cu(MeCN)_4]PF_6$ (18.6 mg, 0.05 mmol) was added to an acetone solution (10.0 cm^3) containing Hcmp (26.8 mg, 0.20 mmol). The solution was stirred and filtered, and the colourless filtrate was transferred to a 10 mm diameter glass tube and layered with 1.0 cm^3 of *n*-pentane as a diffusion solvent. After standing for one month at ambient temperature colourless brick crystals were isolated (Found: C, 58.50; H, 5.00; N, 16.50. Calc. for $C_{33}H_{35}CuN_8O_4$: C, 59.05; H, 5.20; N, 16.70%).

$[Cu_2(Hcmp)_4(Me_2CO)_2][BF_4]_2$ 2. The colourless brick crystals of compound **2** were prepared at room temperature by diffusion of *n*-pentane into an acetone solution (4.0 cm^3) containing $[Cu(MeCN)_4]BF_4$ (12.6 mg, 0.04 mmol) and Hcmp (10.8 mg, 0.08 mmol) (Found: C, 42.15; H, 3.55; N, 11.90. Calc. for $C_{17}H_{18}BCuF_4N_4O_3$: C, 42.80; H, 3.80; N, 11.75%).

$[Cu_5(cmp)_4]ClO_4$ 3. Copper(II) perchlorate hexahydrate (37.1 mg, 0.10 mmol) and copper plates (3 × 3 × 1 mm, five pieces) were stirred in 10.0 cm^3 of EtOH under an ethene atmosphere for 1 h, and to the resultant colourless solution was added an acetone solution (5.0 cm^3) containing Hcmp (26.8 mg, 0.20

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mmol) under argon. The mixture was stirred and filtered, and the filtrate was transferred to a glass tube and layered with 1.0 cm^3 of diethyl ether as a diffusion solvent. After standing for two weeks at ambient temperature yellow prism crystals were isolated at the interface between the two solutions (Found: C, 34.25; H, 2.30; N, 12.00. Calc. for $C_{28}H_{20}ClCu_5N_8O_8$: C, 35.40; H, 2.10; N, 11.80%).

X-Ray data collection, structure solution and refinement

All the X-ray diffraction experiments were performed at room temperature on a Rigaku AFC-5R four-circle diffractometer equipped with a 12 kW rotating anode Mo X-ray source [$\lambda(K\alpha)$ = 0.710 69 Å]. In the case of compounds **1** and **2**, a suitable single crystal was mounted on a glass fibre coated with paraffin to avoid decomposition in air. A yellow prism crystal of compound **3** was sealed in a glass capillary together with some mother liquor. Unit-cell parameters were obtained from a least-squares analysis of the setting angles of 25 high-angle reflections. Space groups were selected on the basis of systematic absences and intensity statistics. Intensity data were collected by using standard scan techniques (ω–2θ). For **1** and **2**, the intensities of 3 standard reflections, monitored at 150 reflection intervals throughout the data collection, remained constant within experimental error, indicating crystal and electronic stability. Over the course of the data collection for **3**, however, the crystal deteriorated and the reflection intensities decreased appreciably due to instability of the crystal.

The diffracted intensities were corrected for Lorentz, polarization and background effects. An empirical absorption correction using the program DIFABS [19a] was applied for **1** and **2**, which resulted in transmission factors ranging from 0.97 to 1.00 and 0.86 to 1.09, respectively. Azimuthal scans of several reflections for **3** indicated that there was not a need for an absorption correction. The structures were solved by a combination of direct and Fourier-difference methods and refined by full-matrix least squares. The heavy atoms (Cu) were located from an e map calculated by the program MITHRIL.[19b] The remaining non-hydrogen atoms were found by direct-method phase-refinement techniques (DIRDIF).[20] The positions of all the hydrogen atoms for **1** and **2** were determined from difference electron-density maps and included in the refinement. The final refinements for these two structures were performed on these data having $I > 3\sigma(I)$ and included anisotropic thermal parameters for all non-hydrogen atoms. During the refinement of **3** only five copper atoms were allowed anisotropic thermal motion and the hydrogen atoms at their calculated positions (C–H 0.95 Å) were not added to the subsequent structure-factor calculations. The counter anion ClO_4^- could not be precisely located due to its high disorder and several peaks of *ca.* 1.49 e $Å^{-3}$ were located near the open channels in the structure. All these factors contribute to a high R value and poor agreement between F_o and F_c values of some low-order reflections. Nevertheless, the overall chemical features of **3** were well enough defined though the accuracy of the metrical parameters is low. Reliability factors are defined as $R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. Atomic-scattering factors and anomalous dispersion terms were taken from the usual sources.[21] All crystallographic computations were performed on a VAX computer by using the program system TEXSAN.[22] Details of the X-ray experiments and crystal data for the three complexes are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/12.

Results and Discussion

Infrared spectroscopy

Infrared spectroscopy can give reliable information on the presence in a sample of any polyatomic anions such as ClO_4^-, PF_6^- and BF_4^-.[23] The IR spectra of complexes **1**–**3** in Fig. 1 show the different absorption characteristics. All three compounds show ν(CN) and ν(C=O) stretchings indicative of the presence of the Hcmp or cmp ligand. Complexes **2** and **3** show ν(BF) and ν(OCl) at 1030 and 1100 cm^{-1}, respectively, whereas **1** does not show the band expected for the PF_6^- anion although $[Cu(MeCN)_4]PF_6$ was used as a source of metal ion in the preparation of the complex. This leaves little doubt that one of the Hcmp molecules in **1** is deprotonated to balance electrical charge. On the other hand, both **1** and **2** show the ν(NH) stretching frequency in the region 2900–3000 cm^{-1}; this absorption is completely missing in **3** indicating that the ligand in this complex exists as the cmp monoanion rather than as

Table 1 Crystal and refinement data for complexes **1**–**3**

	1	**2**	**3**
Formula	$C_{33}H_{35}CuN_8O_4$	$C_{17}H_{18}BCuF_4N_4O_3$	$C_{28}H_{20}ClCu_5N_8O_8$
M	670.96	476.70	949.70
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	$I\bar{4}$	$P2_1/c$	$P2_1/n$
a/Å	17.051(4)	6.783(9)	13.172(4)
b/Å	17.051(4)	23.328(5)	19.849(4)
c/Å	5.203(7)	13.440(3)	20.912(5)
β/°	90.0	97.77(4)	102.06(2)
U/$Å^3$	1513(2)	2107(2)	5346(2)
D_c/g cm^{-3}	1.449	1.5034	1.180
Z	2	4	4
Crystal size/mm	0.30 × 0.30 × 0.40	0.15 × 0.15 × 0.15	0.15 × 0.15 × 0.25
F(000)	678.0	968.0	1880.0
μ(Mo-Kα)/cm^{-1}	7.72	10.96	20.45
Scan speed/° min^{-1}	2.0	8.0	16.0
Scan width/°	1.50 + 0.30 tan θ	1.00 + 0.30 tan θ	1.00 + 0.30 tan θ
No. reflections measured	1020	4730	5770
No. observations [$I > 3.00\sigma(I)$]	831	1360	1187
No. parameters	104	226	211
R	0.077	0.067	0.118
R'	0.093	0.065	0.187
Goodness-of-fit	3.54	1.89	6.49

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**–**3**

Complex **1**			
Cu–N(1)	1.978(8)		
N(1)–Cu–N(1′)	111.2(2)	N(1)–Cu–N(1″)	106.1(5)
Complex **2**			
Cu–O(3)	2.253(9)	Cu–O(3′)	2.457(9)
Cu–N(1)	1.859(9)	Cu–N(3)	1.87(1)
Cu • • • Cu′	3.379(5)		
N(1)–Cu–N(3)	159.6(4)	N(1)–Cu–O(3′)	101.8(4)
N(1)–Cu–O(3)	95.0(3)	O(3)–Cu–O(3′)	88.4(2)
N(3)–Cu–O(3′)	97.7(4)	N(3)–Cu–O(3)	91.4(4)
Complex **3**			
Cu(1)–Cu(2)	2.63(1)	Cu(1)–Cu(4)	2.70(1)
Cu(2)–Cu(3)	2.69(1)	Cu(3)–Cu(4)	2.66(1)
Cu(1)–O(3)	1.87(4)	Cu(1)–N(2)	1.93(5)
Cu(2)–O(1)	1.85(4)	Cu(2)–N(8)	1.85(5)
Cu(3)–O(4)	1.85(4)	Cu(3)–N(4)	1.92(5)
Cu(4)–O(2)	1.80(4)	Cu(4)–N(6)	1.82(4)
Cu(5)–N(1′)	1.83(5)	Cu(5)–N(3′)	2.08(6)
Cu(5)–N(5)	1.92(5)	Cu(5)–N(7′)	2.04(5)
Cu(2)–Cu(1)–Cu(4)	95.8(3)	Cu(1)–Cu(4)–Cu(3)	81.2(3)
Cu(1)–Cu(2)–Cu(3)	81.8(3)	Cu(2)–Cu(3)–Cu(4)	95.2(4)
O(3)–Cu(1)–N(2)	169(2)	Cu(2)–Cu(1)–O(3)	99(1)
Cu(2)–Cu(1)–N(2)	87(1)	Cu(4)–Cu(1)–O(3)	80(1)
Cu(4)–Cu(1)–N(2)	108(1)	O(1)–Cu(2)–N(8)	179(2)
Cu(1)–Cu(2)–N(8)	99(1)	Cu(1)–Cu(2)–O(1)	82(1)
Cu(3)–Cu(2)–O(1)	93(1)	Cu(3)–Cu(2)–N(8)	87(1)
O(4)–Cu(3)–N(4)	171(2)	Cu(2)–Cu(3)–N(4)	109(1)
Cu(2)–Cu(3)–O(4)	79(1)	Cu(4)–Cu(3)–N(4)	85(1)
Cu(4)–Cu(3)–O(4)	98(1)	O(2)–Cu(4)–N(6)	178(2)
Cu(1)–Cu(4)–N(6)	87(1)	Cu(1)–Cu(4)–O(2)	95(1)
Cu(3)–Cu(4)–N(6)	100(1)	Cu(3)–Cu(4)–O(2)	81(1)
N(1′)–Cu(5)–N(3′)	115(2)	N(1′)–Cu(5)–N(5)	114(2)
N(1′)–Cu(5)–N(7′)	107(2)	N(3′)–Cu(5)–N(5)	108(2)
N(3′)–Cu(5)–N(7′)	98(2)	N(5)–Cu(5)–N(7′)	113(2)

neutral Hcmp. The IR spectra together with the determined structures for the three compounds are consistent with the suggested stoichiometries.

Crystal structure of [Cu(cmp)(Hcmp)$_3$]·C$_5$H$_{12}$ 1

The compound was formulated on the basis of the total elemental analysis and a single-crystal X-ray structure determination. The structure of complex **1** contains a hydrogen-bonded framework that is composed of a copper Hcmp complex as shown in Fig. 2. The copper(I) ion in the monomeric unit [Cu(cmp)(Hcmp)$_3$] is tetrahedrally co-ordinated to four cyano groups of one cmp and three Hcmp molecules with N–Cu–N angles of 111.2(2) and 106.1(5)°. As the precise position of the deprotonated NH group from one of the four Hcmp molecules cannot be determined the structure presented below is an average result. The metal centre occupies a crystallographic $\bar{4}$ position and hence all Cu–N bonds are identical, being 1.978(8) Å. Each Hcmp moiety is further head-to-tail hydrogen bonded to two adjacent Hcmp groups belonging to other units through the pyridone N and O atoms. Since there is not any difference crystallographically between cmp and Hcmp due to rapid transition of the protons, each [Cu(cmp)(Hcmp)$_3$] entity is essentially connected to eight others. The dihedral angle between the two hydrogen-bonded Hcmp groups is 84.43°, and this results in four monomeric units interconnected through hydrogen bonds forming an open cavity, Fig. 2. Each supramolecular cavity thus generated includes one *n*-pentane as the guest molecule. The three-dimensional frames contain four-connected (the Cu atoms) and three-connected (the ligands) centres in the ratio 1:4. The topological type can be confirmed by placing a nodal point at the centres of the ligands and correctly connecting all the metallic and organic centres. The resulting frame can be related to the uniform three-dimensional net $(8,\frac{3}{4})$ described by Wells,[24] where 4 and 3 are the number of links meeting at each point for M and L, respectively, and 8 is the number of points in the smallest circuits. The overall structure is made of such repeating units leading to the infinite channels running parallel to the *c* axis (Plate 1).

Crystal structure of [Cu$_2$(Hcmp)$_4$(Me$_2$CO)$_2$][BF$_4$]$_2$ 2

The molecular structure of complex **2** exists in the solid state as a polymer of weakly bound dimers. Within the dimer, each copper(I) ion has a distorted-tetrahedral geometry comprising two cyano nitrogen atoms of the Hcmp groups and two acetone molecules, Fig. 3. The two metal centres are linked by the unusual bridging of acetone forming a weakly coupled dimeric Cu$_2$N$_4$O$_2$ chromophore. The relatively long Cu • • • Cu separation of 3.379(5) Å precludes any metal–metal interactions. The Cu–O(3) distance of 2.253(9) Å is slightly shorter than the corresponding Cu–O bond length of 2.31 Å in the dimeric copper(I) acetate structure,[25] while the Cu–O(3′) separation of 2.457(9) Å is comparable with those reported for the weak interaction between the Cu(I) ion and the oxygen atoms of the ClO$_4^-$ anion in [Cu(bipy)(CH$_2$=CHPh)]ClO$_4$ (bipy = 2,2′-bipyridine) [2.591(4) Å][26] and [Cu(μ-vpy)$_2$(vpy)$_2$][ClO$_4$]$_2$ (vpy = 2-vinylpyridine) [2.773(16) Å].[27]

Each Hcmp in a dimeric unit is hydrogen-bonded pairwise to

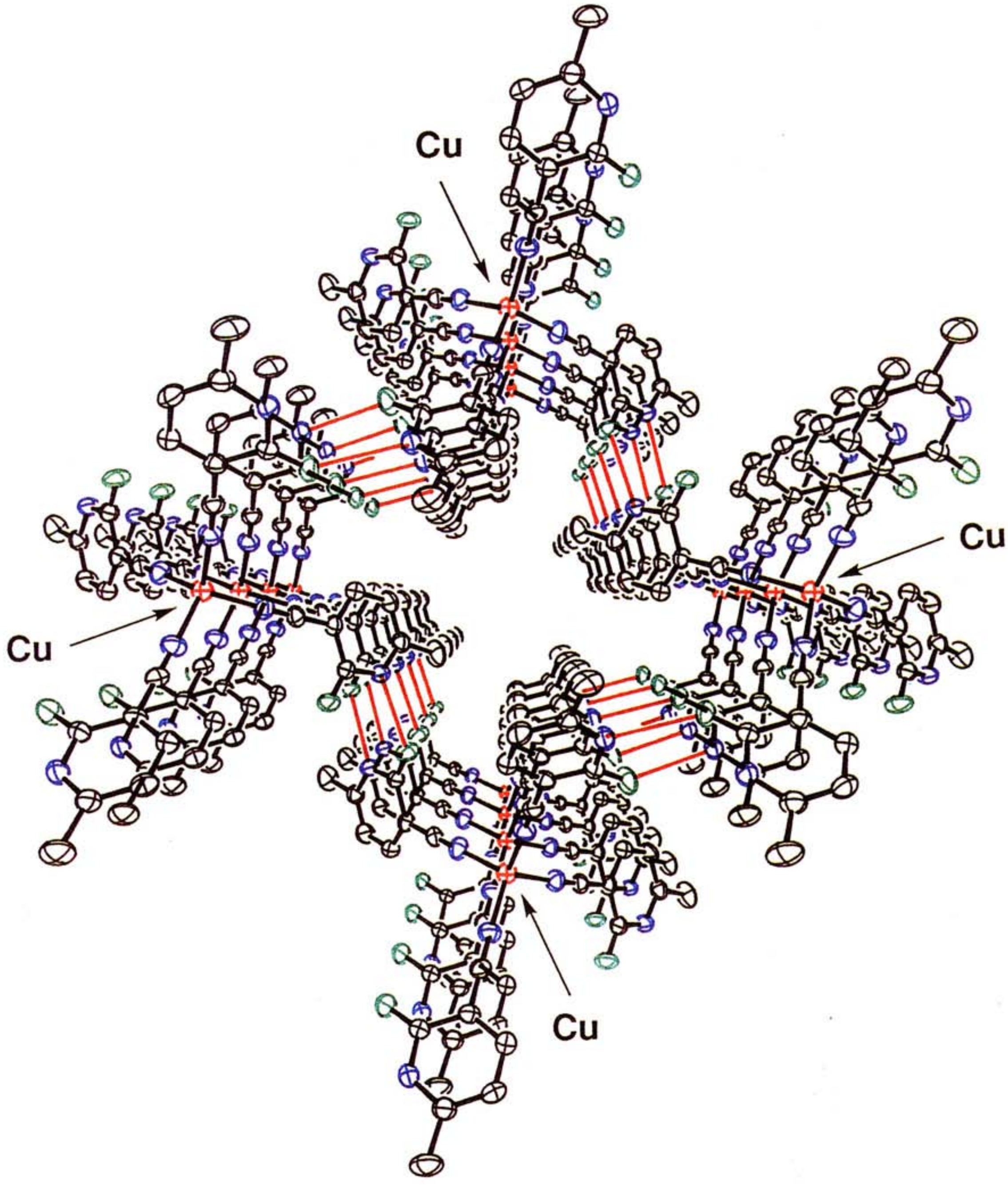

Plate 1 Perspective view along the *c* axis of the supramolecular square channels in complex **1**. Hydrogen bonds are shown in red and the copper, nitrogen and oxygen atoms in red, blue and green respectively

only one adjacent Hcmp molecule (rather than two as in complex **1**) belonging to the other dimer in a head-to-tail mode with the dihedral angle between the two pyridone rings of 2.58° and the N $\cdots$ O distances of 2.78(1) and 2.701(9) Å. This results in a one-dimensional array of copper atoms along the *c* axis, Fig. 4. Within the dimer the closest interplane separation between the two coupled Hcmp groups is 4.0 Å, indicative that π–π interaction between the pyridone rings in this complex is not the major intermolecular force for association of two monomeric units into a dimeric structure.[15]

Crystal structure of $[Cu_5(cmp)_4]ClO_4$ 3

The supramolecular structure of complex **3** is composed of $[Cu_5(cmp)_4]ClO_4$ units, each of which involves two types of metal atoms as illustrated in Fig. 5. The first type contains a Cu_4 cluster comprising Cu(1), Cu(2), Cu(3) and Cu(4). If the Cu–Cu separations of 2.63–2.70 Å are excluded as bonding, each Cu atom involves a nearly linear OCuN chromophore made up of one O and one N atom from two different cmp groups. The O–Cu–N angles for the four copper atoms range from 169(2) to 179(2)°. Thus, each cmp group connects two separate copper atoms through pyridone N and O atoms and this results in four copper centres interconnected with Cu(1) and Cu(3) 0.216 Å above, and Cu(2) and Cu(4) 0.211 Å below, the 'equatorial plane'. Thus, the Cu_4 cluster can be best considered as a butterfly configuration similar to that in the tetranuclear copper(I) complex $[\{Cu(NEt_2)\}_4]$.[28] While a number of examples are known where bridging ligands lead to polymetallic copper(I) clusters with relatively short Cu $\cdots$ Cu distances,[29] it is still a matter of some controversy in partition of these copper–copper distances into bonding and non-bonding. Nevertheless, the short Cu–Cu distances in complex **3** may be compared with the corresponding distance of 2.56 Å in copper metal.

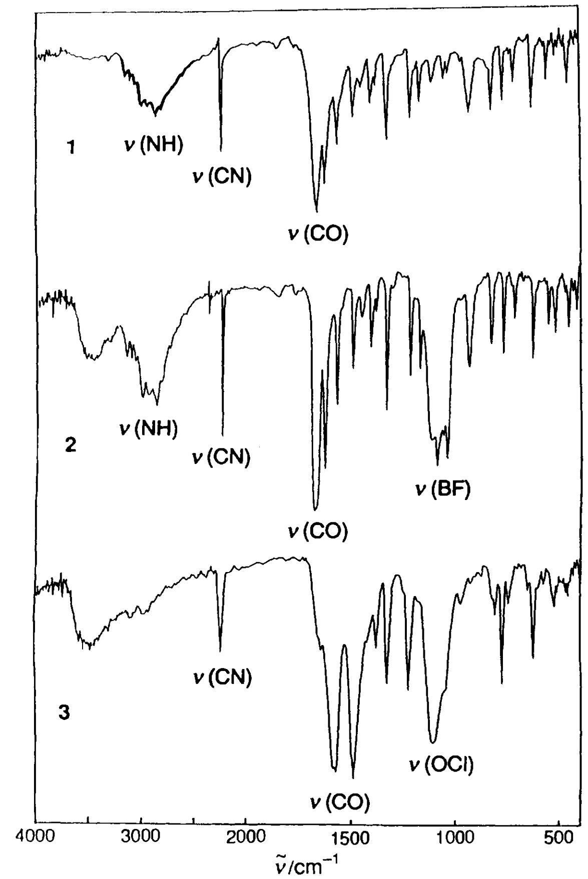

Fig. 1 IR spectra for the complexes **1**–**3** over the range 400–4000 cm^{-1}

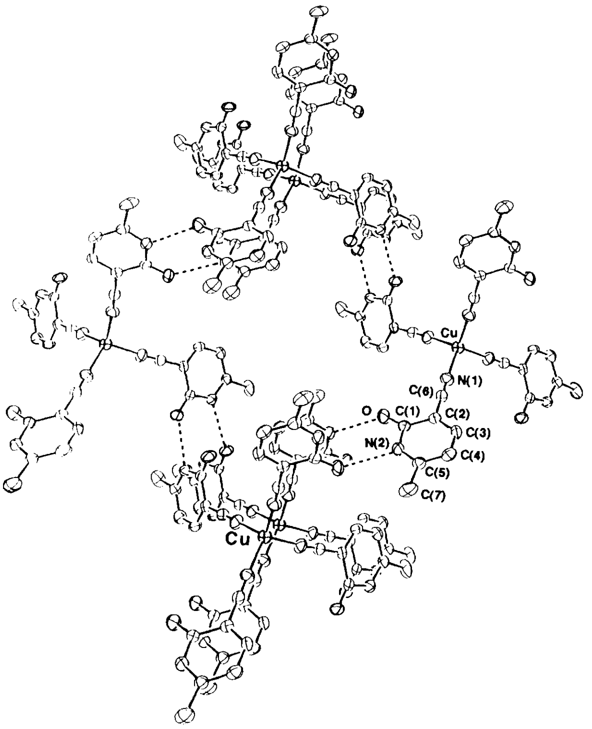

Fig. 2 Perspective view of the molecular structure of complex **1** showing the four [Cu(cmp)(Hcmp)$_3$] monomers interlinked by hydrogen bonds (broken lines) to form a cavity. The inclusion molecule is omitted for clarity

The Cu(5) ion and its symmetry-related equivalents belong to the second category of copper(I) atoms, each involving a tetrahedral co-ordination environment comprising four N atoms of the CN group from four different cmp moieties. Thus, each cmp monoanion employs all its three functional groups bridging three copper atoms forming a supramolecular channel architecture as shown in Plate 2 with the large rectangular channels essentially empty.

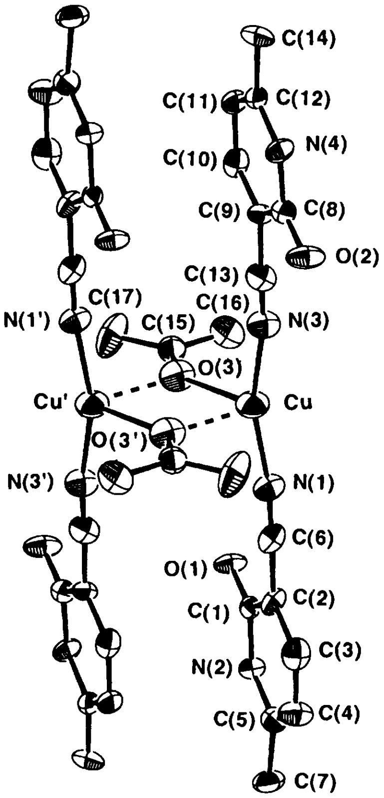

Fig. 3 Molecular structure of the weakly bound dimeric unit in complex **2**

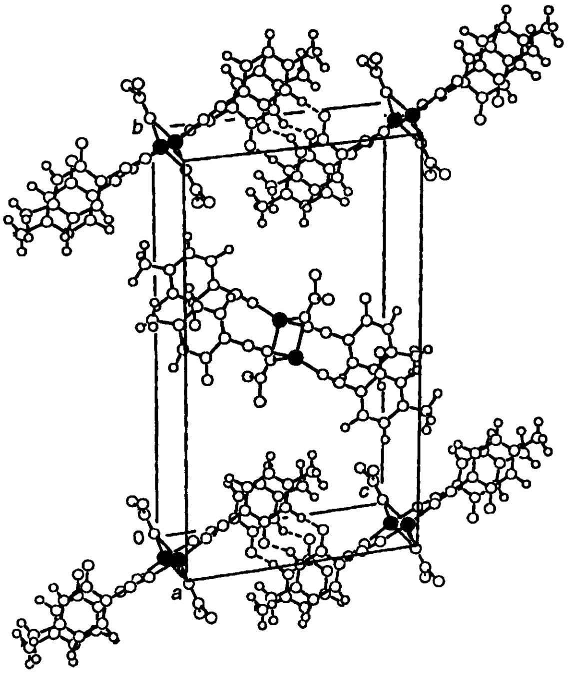

Fig. 4 Unit-cell packing diagram for complex **2**. Hydrogen bonds are indicated by broken lines

As stated earlier, the high *R* value for this complex is a direct consequence of the unstable nature of the material. The single crystal used for X-ray diffraction was sealed in a capillary with a little mother-liquor. The diffusion solvent Et$_2$O might occupy the above discussed micropores in the compound. During data

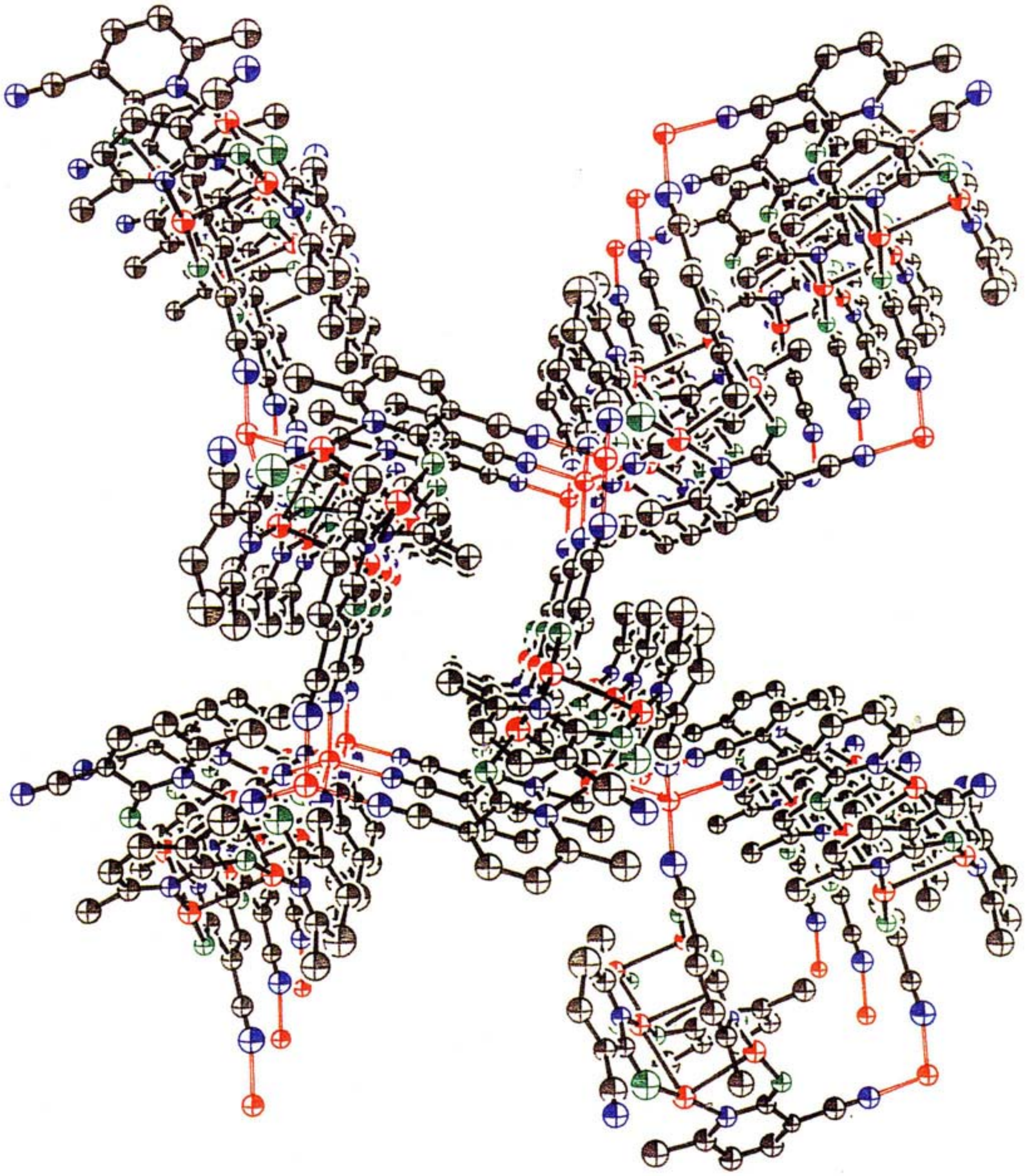

Plate 2 Perspective view of the supramolecular rectangular channel framework in **3** formed by tridentate co-ordination of cmp. The copper, nitrogen and oxygen atoms are shown in red, blue and green respectively. The co-ordination bonds involving the cyano nitrogen atoms are red and those involving the pyridone nitrogen and oxygen atoms black

collection these loosely hosted solvent molecules might leave the cavities causing deterioration of the crystal and reduction of reflection intensities. This suggests that in the absence of guest molecules the inclusion lattice cannot be effectively maintained. Nevertheless, the framework and the channel structure containing a Cu_4 cluster it generates are the aspects of major interest and the overall chemical features of the compound are beyond any doubt.

Channel networks in complexes 1 and 3

It is interesting to note that in complex **3** hydrogen bonding is not involved. Instead, the supramolecular architecture is built up by the tridentate co-ordination of the deprotonated Hcmp molecules. Recent publications reveal several such notable examples of three-dimensional networks formed by metal cations linked through linear bidentate organic ligands.[7–9] We consider that tridentate ligands such as cmp might have a similar profound significance in the design and construction of unique channel structures in other systems. On the other hand, compound **1** presented in this work is a novel member of the limited family of hydrogen-bonded supramolecular co-ordination compounds.[12,13] The most remarkable structural feature of this complex is that it involves a square channel architecture rather than the frequently observed honeycomb frameworks as in cadmium cyanide,[7] silver(I)–phenazine,[15a] copper(I)–benzothiadiazole[15b] and copper(I)–pyrazine[9] systems, or a helical channel structure as in the hydrogen-bonded pimelic acid polymeric structure.[4b] To the best of our knowledge, complex **1** represents the first example of an inorganic supramolecular structure with a three-dimensional square channel lattice linked by hydrogen bonds. This demonstrates that inorganic supramolecular architectures can be constructed and stabilized without covalent modification of the tecton.[13]

Whereas the rectangular channel networks observed in complex **3** were known before this work,[5,6] a three-dimensional polymer containing metal clusters is a novel structure. There is only one similar example reported for a succinatodisilver(I) complex $[Ag_2\{O_2C(CH_2)_2CO_2\}]$.[10] A significant feature of this compound and **3** is that they might constitute a link between purely inorganic solids and extended cation aggregates and molecular clusters. Above all, the channel structures

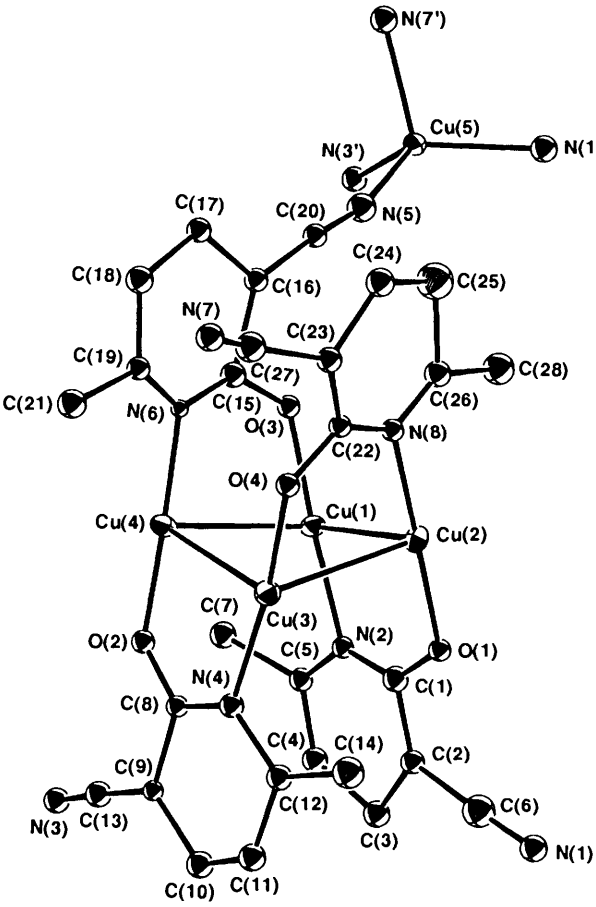

Fig. 5 Molecular structure of the $[Cu_5(cmp)_4]ClO_4$ unit in complex **3** with the atom-numbering scheme

observed in complexes **1** and **3**, like the materials with microchannels and micropores, can also be viewed as composed of host frameworks and might have potential properties in the area of host–guest chemistry similar to zeolites.[5,30] The design of numerous other supramolecular systems and processes with hydrogen bonding or using similar tridentate ligands as molecular building blocks is under way.

Acknowledgements

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