

Directed assembly of dinuclear and mononuclear copper(II)-carboxylates into infinite 1-D motifs using isonicotinamide as a high-yielding supramolecular reagent

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Isonicotinamide has been employed as a supramolecular reagent in the synthesis of five Cu(II) complexes, tetrakis(μ -acetato-*O,O'*)-bis(isonicotinamide-*N*)dicopper(II) acetonitrile; *trans*-diaquabis(2-fluorobenzoato-*O*)-bis(isonicotinamide-*N*)copper(II), bis{bis(μ_2 -acetato-*O*-acetic acid-*O*-bis(isonicotinamide-*N*)copper(II)) bis(methanol), bis(acetato-*O*-acetic acid-*O*-bis(isonicotinamide-*N*)copper(II) acetic acid, bis(2-fluorobenzoato-*O*)-2-fluorobenzoic acid-*O*-bis(isonicotinamide-*N*)copper(II). The crystal structure determination of these compounds demonstrate that an effective supramolecular reagent can be combined with very different (chemically and structurally) inorganic building blocks and still create a family of inorganic–organic hybrid materials that all display the same principal supramolecular motifs; infinite 1-D chains. This consistency (which can be equated with a high supramolecular synthetic ‘yield’) has been achieved in the presence of several potentially disruptive (in a structural sense) molecules, *e.g.* water, methanol, and acetic acid. This illustrates that flexible or unpredictable coordination chemistry does not, in itself, necessarily prevent supramolecular synthesis using a reliable supramolecular reagent, in this case the structurally bifunctional isonicotinamide ligand.

Introduction

Crystal engineering^{1,2} has focused primarily on the syntheses of (i) extended organic networks (notably using hydrogen bonds),^{3–5} and (ii) transition-metal based coordination polymers (relying on coordinate covalent bonds).^{6,7} Much less work has been done on the construction of inorganic–organic hybrid materials with intermolecular forces.⁸ The synthetic tools available for the construction of such assemblies are non-covalent interactions, many of which are poorly understood and difficult to calculate and measure. Consequently, controlling the properties of a solid through precise control over its crystal structure or principal structural motifs is a formidable task. The good news is that many assemblies and structural patterns have been constructed through intermolecular interactions, and the use of molecules or ions (instead of atoms) as building blocks of functional solids and ordered networks has become an important synthetic strategy in chemistry and materials science.

Composite hybrid materials are of crucial importance in natural systems⁹ but the combination of organic ligands and transition-metal ions also brings together synthetic flexibility (from the principles of organic chemistry) and properties and reactivities inherent in metal ions. The reasons for incorporating metal ions into supramolecular networks are numerous; metal ions give access to physical properties that are less common in organic solids *e.g.* magnetic properties, conductivity, and catalytic activity (metal complexes with hydrogen-bonding capabilities may also be used as chemotherapeutic compounds).¹⁰ Metal ions also display a range of coordination geometries allowing for greater flexibility in constructing materials with specific dimensions and topologies. Supramolecular synthesis of metal-containing materials has primarily been achieved by coordinating bifunctional ligands such as 4,4'-bipyridine to metal ions.^{11–14} Some examples include

pyrazine and Cu(II) ions to produce a 2-D network with rectangular channels,¹⁵ and similar 2-D square networks with open channels have been constructed from Zn(II)¹² or Cd(II)¹⁶ and 4,4'-bpy. Other examples include Ag(I) helicates,¹⁷ circular double helicates,¹⁸ supramolecular macrocycles,¹⁹ zinc(II) porphyrins assembled into cages,²⁰ and a large number of interpenetrating diamondoid structures.²¹

Only recently have non-covalent interactions (notably hydrogen bonds) been used in a deliberate strategy for connecting metal complexes into extended networks.^{22–26} The inherent coordination geometry of the metal ion can be propagated through ligand-based hydrogen-bond interactions into a specific supramolecular architecture which demonstrates that hydrogen bonds working in concert are capable of ‘manoeuvring’ substantial complex ions into desirable motifs, even in the presence of competing cation–anion, solvent–metal, and solvent–solvent interactions.

Effective supramolecular synthesis requires non-covalent intermolecular forces that consistently form reliable and specific motifs even in the presence of potentially disrupting counterions, solvent molecules, and other chemical or geometric variables. This is particularly important in the design on new functional materials where a desirable physical property is crucially dependent upon an optimum three-dimensional structure. In the context of molecular-based magnet materials, Cu(II) has played a prominent role, both in experimental and theoretical studies.²⁷ Unfortunately (from the point of view of structural consistency) Cu(II) displays a very varied and unpredictable coordination chemistry, which makes it all the more difficult to incorporate such ions into extended assemblies with predetermined topology and connectivity.

In this paper we demonstrate how isonicotinamide can be employed as a practical ‘supramolecular reagent’, an effective tool for consistently assembling coordination complexes of

Cu(II), with widely differing geometries and ligands, into infinite 1-D chains. The supramolecular synthetic strategy employed here combines the metal-coordinating ability of pyridine and the robust self-complementary hydrogen-bonding ability of the amide functionality.²⁸ This approach allows for the repeated construction of infinite 1-D motifs containing either mononuclear or dinuclear copper(II) coordination complexes as illustrated by the crystal structures of tetrakis(μ -acetato-*O,O'*)-bis(isonicotinamide-*N*)-dicopper(II) acetonitrile **1**, *trans*-diaqua-bis(2-fluorobenzoato-*O*)-bis(isonicotinamide-*N*)copper(II) **2**, bis{bis(μ_2 -acetato-*O*)-acetic acid-*O*-bis(isonicotinamide-*N*)copper(II)} bis(methanol) **3**, bis(acetato-*O*)-acetic acid-*O*-bis(isonicotinamide-*N*)copper(II) acetic acid **4**, and bis(2-fluorobenzoato-*O*)-2-fluorobenzoic acid-*O*-bis(isonicotinamide-*N*), **5**.

Experimental

Preparation of **1**

A solution of isonicotinamide (0.40 g, 3.2 mmol) in acetonitrile was added to a solution of copper(II) acetate in acetonitrile (0.050 g, 0.25 mmol) with a few drops of glacial acetic acid (to obtain a clear solution). The mixture was heated for fifteen minutes and left to stand at ambient temperature, blue-green crystals of **1** appeared overnight. Repeated recrystallization from acetonitrile with a few drops of acetic acid produced crystals suitable for single-crystal X-ray diffraction.

Preparation of **2**

Blue crystals of **2** were obtained either from the same solution as **5** or by recrystallisation of **5** in water.

Preparation of **3**

A solution of isonicotinamide (0.40 g, 3.2 mmol) in methanol was added to a solution of copper(II) acetate in methanol (0.050 g, 0.25 mmol) with a few drops of glacial acetic acid (to obtain a clear solution). The mixture was heated for fifteen minutes and left to stand at ambient temperature, blue crystals of **3** suitable for single-crystal X-ray diffraction appeared overnight.

Preparation of **4**

A 5 mL aliquot of the mother liquor of **1** was added to a vial. The vial was tightly capped and left undisturbed at -20 °C. After several days, blue crystals of **4** appeared.

Preparation of **5**

Copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) (0.24 mg, 1.0 mmol) was dissolved in 3.5 mL of methanol with stirring. 2-Fluorobenzoic acid (0.28 g 2.0 mmol) was dissolved in methanol (30 mL) and added to the methanolic copper solution resulting in a light-green color. Isonicotinamide (0.49 g 4.0 mmol) dissolved in methanol (10 mL) was added to the solution, whereupon the color changed to blue. The mixture was then heated for fifteen minutes. The solution obtained was left to stand at room temperature. Clear blue crystals of **5** precipitated first followed by the appearance of blue crystals of **2**.

X-Ray crystallography

Crystalline samples of **1–5** were placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated using a Bruker SMART 1000 system, with graphite monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation at 223 K. The structures were solved by direct methods using SHELXS-97 and refined using

SHELXL-97.²⁹ Non-hydrogen atoms were found by successive full matrix least squares refinement on F^2 and refined with anisotropic thermal parameters. Hydrogen atom positions were located from difference Fourier maps and a riding model with fixed thermal parameters [$u_{ij} = 1.2U_{ij}(\text{eq})$ for the atom to which they are bonded] was used for subsequent refinements. Table 1 provides crystallographic details for **1–5**, and the molecular geometries and numbering scheme are shown in Figs. 1a–e.

CCDC reference numbers 215919–215923.

See <http://www.rsc.org/suppdata/dt/b3/b308446a/> for crystallographic data in CIF or other electronic format.

Magnetic measurements

Magnetic measurements were carried out using a Quantum Design MPMS5 SQUID magnetometer with maximum applied field of 55 kOe. Samples in powder form were packed in plastic capsules and the measurements were performed under flowing He gas.

Results

The crystal structure of **1** contains the commonly occurring dinuclear ('paddlewheel')copper(II) unit constructed by four bridging acetate ligands, Table 2. The 'peripheral' coordination site on each ion is occupied by an isonicotinamide ligand (coordination through the pyridine nitrogen atom). This arrangement means that the two amide functionalities are oriented in a linear fashion but pointing in opposite directions. Each amide moiety forms two symmetry related N–H \cdots O hydrogen bonds, Table 3, with an adjacent metal complex, resulting in infinite linear chains of ions, Fig. 2. Neighbouring chains are arranged in a parallel manner although there are no strong hydrogen bonds between chains.

The remaining N–H proton on each amide functionality forms an N–H \cdots N hydrogen bond ($r(\text{N} \cdots \text{N})$ 3.07 Å) to the included acetonitrile. The Cu \cdots Cu separation within the dinuclear core is 2.61 Å, and the Cu \cdots Cu distance between adjacent metal-complexes within each hydrogen-bonded chain is 17.0 Å. The shortest through-space inter-chain distance between Cu(II) ions is 6.2 Å.

The crystal structure of **2** contains copper(II) ions in an elongated tetragonal octahedral (4 + 2) coordination geometry, with two molecules of water and isonicotinamide and two 2-fluorobenzoate ions, all coordinated in a *trans* fashion, Table 2. There are no bridging or chelating ligands; this is a mononuclear species. As in the crystal structure of **1**, the two isonicotinamide ligands act as conventional ligands (through the pyridine nitrogen atom) and as supramolecular reagents through self-complementary N–H \cdots O hydrogen-bond interactions, Fig. 3, Table 3.

As well as being weakly coordinated to the metal-ion ($r(\text{O} \cdots \text{Cu})$ 2.65 Å) the water molecule also acts as a hydrogen-bond acceptor for an *anti*-amide proton and as an intramolecular hydrogen-bond donor to a non-coordinated carboxylate oxygen atom. The water molecules effectively act as bridges between parallel hydrogen-bonded chains, Fig. 4.

The Cu \cdots Cu distance between adjacent metal-ions within each hydrogen-bonded chain is 16.8 Å. The shortest through-space inter-chain Cu \cdots Cu distance is 7.5 Å.

The copper(II) ions in **3** are coordinated to two isonicotinamide ligands and two acetate ions in a plane in a *trans*-geometry, with a third acetate ion completing a near-perfect (4 + 1) square pyramidal arrangement ($\tau = 0.00$),³⁰ Table 2. Two of the acetate ions coordinate to neighbouring copper ions in a μ_2 -manner which creates a dinuclear species with a Cu \cdots Cu separation of 3.5 Å. These dinuclear building blocks are subsequently extended into two infinite parallel chains *via* the self-

Table 1 Crystallographic details for 1–5

	1	2	3	4	5
Systematic name	(C ₆ H ₆ N ₂ O)(C ₂ H ₃ O ₂) ₂ (C ₂ H ₃ N) ₂ Cu	(C ₆ H ₆ N ₂ O) ₂ (C ₇ H ₄ O ₂ F) ₂ (OH) ₂ Cu	(C ₆ H ₆ N ₂ O) ₂ (C ₂ H ₃ O ₂) ₂ (CH ₄ O) _{1.25} Cu	(C ₆ H ₆ N ₂ O) ₂ (C ₂ H ₃ O ₂) ₂ (C ₂ H ₄ O) ₂ Cu	(C ₆ H ₆ N ₂ O) ₂ (C ₇ H ₄ O ₂ F) ₂ (C ₇ H ₅ O ₂ F)Cu
Empirical formula	C ₁₂ H ₁₅ CuN ₃ O ₅	C ₂₆ H ₂₄ CuF ₂ N ₄ O ₈	C _{17.25} H ₂₃ CuN ₄ O _{7.25}	C ₃₀ H ₃₆ CuN ₄ O ₁₀	C ₃₃ H ₃₅ CuF ₃ N ₄ O ₈
Molecular weight	344.81	622.03	465.94	545.99	726.11
Color, habit	Blue-green prism	Blue prism	Blue plate	Blue-green prism	Blue plate
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group, Z	P1̄, 2	P1̄, 1	P1̄, 2	P2(1)/c, 4	P2(1)/c, 4
a/Å	7.200(1)	7.481(1)	9.305(2)	11.040(2)	11.079(1)
b/Å	8.103(1)	7.728(1)	10.154(2)	15.245(2)	19.771(2)
c/Å	13.449(2)	12.586(2)	12.885(2)	15.650(2)	15.528(2)
α/°	90.408(2)	72.762(3)	69.735(3)	90	90
β/°	96.328(3)	72.803(3)	75.696(3)	104.910(3)	104.284(3)
γ/°	96.118(2)	77.970(3)	67.129(3)	90	90
Volume/Å ³	775.2(2)	658.1(2)	1043.4(3)	2545.3(6)	3296.3(7)
Density/g cm ⁻³	1.477	1.57	1.483	1.425	1.463
Temperature/K	203(2)	203(2)	203(2)	203(2)	203(2)
X-ray wavelength	0.71073	0.71073	0.71073	0.71073	0.71073
μ/mm ⁻¹	1.432	0.902	1.094	0.916	0.736
θ _{min} /°	1.52	1.75	2.27	1.9	1.7
θ _{max} /°	28.21	28.32	28.26	28.29	28.12
Reflections					
Collected	5410	4651	7222	17266	21582
Independent	3443	2958	4620	5872	7223
Observed, I > 2σ(I)	3026	2088	3820	4263	4270
R ₁ (observed)	0.0289	0.04	0.0374	0.0359	0.0465
wR ₂ (all)	0.0853	0.091	0.1077	0.107	0.1365

Table 2 Selected bond distances for 1–5

1	Cu1	O3	1.9605(14)
	Cu1	O4	1.9609(15)
	Cu1	O2	1.9749(15)
	Cu1	O1	1.9758(16)
	Cu1	N1	2.1783(16)
2	Cu1	Cu1	2.6111(5)
	Cu1	O17	1.9312(16)
	Cu1	N1	2.0445(19)
3	Cu1	O1S	2.6525(21)
	Cu1	O31	1.9895(16)
	Cu1	N1	2.0227(18)
4	Cu1	N21	2.0270(18)
	Cu1	O31	1.9765(16)
	Cu1	O41	1.9824(14)
5	Cu1	O52	2.5113(17)
	Cu1	N11	1.9944(17)
	Cu1	N21	2.0121(18)
	Cu1	O37	1.936(2)
	Cu1	O58	2.007(2)
	Cu1	N11	2.011(2)
	Cu1	N21	2.022(2)
	Cu1	O48	2.235(2)

complementary, symmetry related, N–H...O interactions between adjacent amide moieties, Fig. 5, Table 3.

The crystal lattice also contains two non-coordinated methanol molecules. Parallel chains are bridged by one methanol molecule that accepts a hydrogen bond from the *anti*-amide proton and donates a hydrogen bond to an uncoordinated carboxylate oxygen atom. The second molecule of methanol is not engaged in any significant intermolecular interactions. The Cu...Cu distance between adjacent metal-ions within each hydrogen-bonded chain is 16.7 Å.

The magnetization in this dinuclear complex was measured as a function of temperature in an applied field of 200 Oe from which the mass susceptibility $\chi(T)$ was determined. The Néel temperature, T_n in the antiferromagnetic susceptibility $\chi(T) = C/(T + T_n)$,³¹ and the effective moment per formula unit, μ , were determined from a Curie–Weiss analysis of magnetic susceptibility data.³² We find T_n of 0.7 (± 0.1) K and μ of 1.66 (± 0.05) μ_B (ground state is a singlet). This type of magnetic behavior is expected for a Cu–O–Cu moiety with a bridging angle of 103.3° (the μ -oxo being part of a carboxylate unit), Fig. 6.³³

The crystal structure of 4 has an unexpected chemical composition with two isonicotinamide ligands and two acetate ions in a plane in a *trans*-geometry, with a molecule of acetic acid completing a (4 + 1) square pyramidal arrangement ($\tau = 0.06$) around the metal ion, Table 2. The coordinated acetic acid also forms an intramolecular hydrogen bond to a coordinated acetate ion. A second molecule of acetic acid (which is not coordinated to the metal ion), forms a hydrogen bond to a coordinated acetate ligand. Despite the complexity of these intermolecular interactions, the desired amide–amide hydrogen bonds prevail, and the result is infinite chains of linearly organized copper(II) complexes. Neighbouring chains are bridged *via* an N–H...O hydrogen bond involving the *anti*-amide proton and an acetate ligand. Fig. 7, Table 3.

The Cu...Cu distance between adjacent metal-ions within each hydrogen-bonded chain is 16.7 Å. The shortest through-space inter-chain Cu...Cu distance is 8.1 Å.

The copper(II) ions in 5 are five coordinated in a heavily distorted square pyramidal geometry ($\tau = 0.35$) generated by two isonicotinamide molecules, two benzoate ions, and one neutral molecule of 2-fluorobenzoic acid, Table 2. The expected amide–amide interaction is observed leading to infinite hydrogen-bonded infinite chains, Fig. 8, Table 3.

The Cu...Cu distance between adjacent metal-ions within each hydrogen-bonded chain is 16.7 Å. The shortest through-space inter-chain Cu...Cu distance is 8.1 Å.

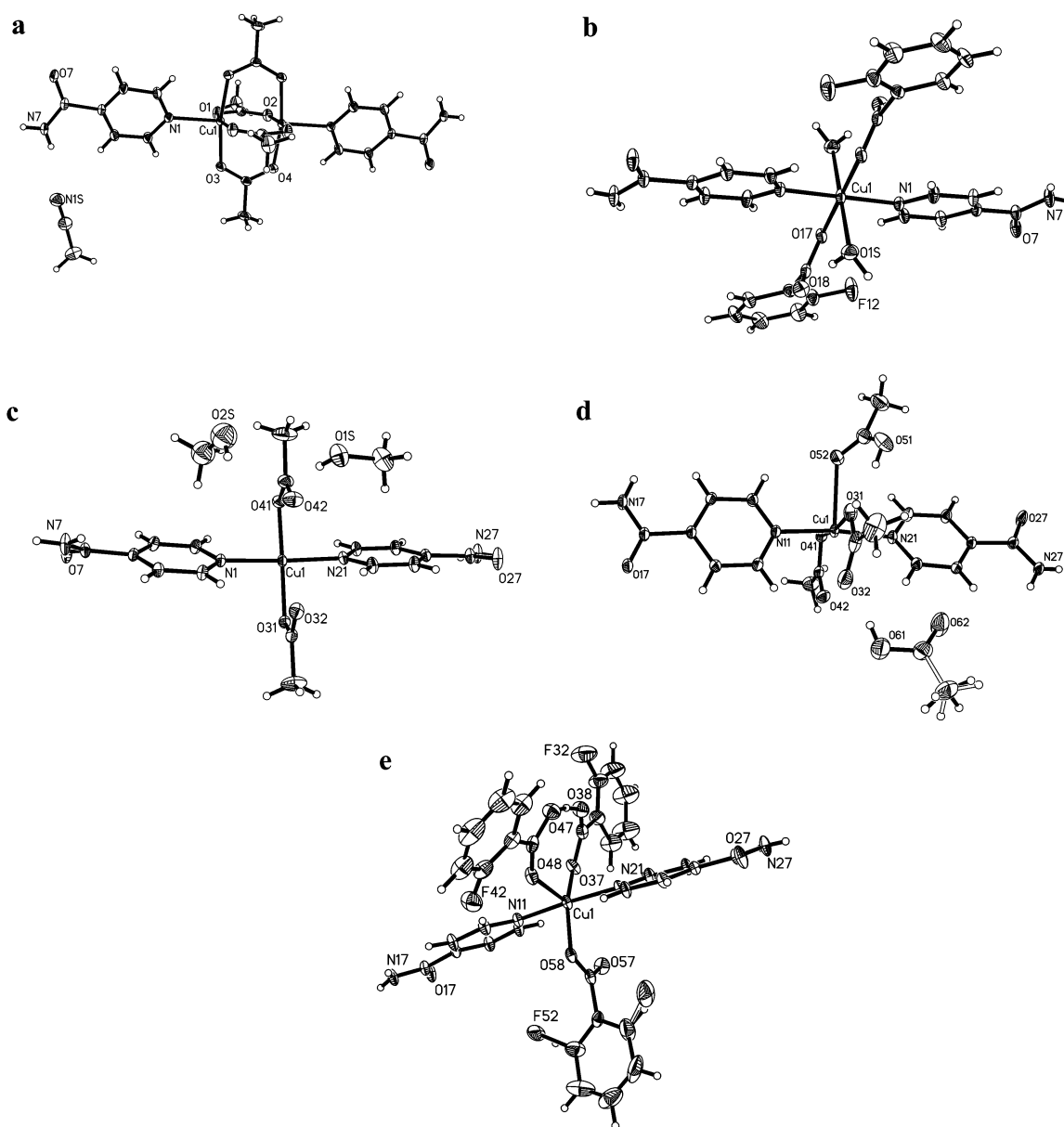


Fig. 1 Molecular geometries, thermal ellipsoids, and numbering schemes for 1–5.

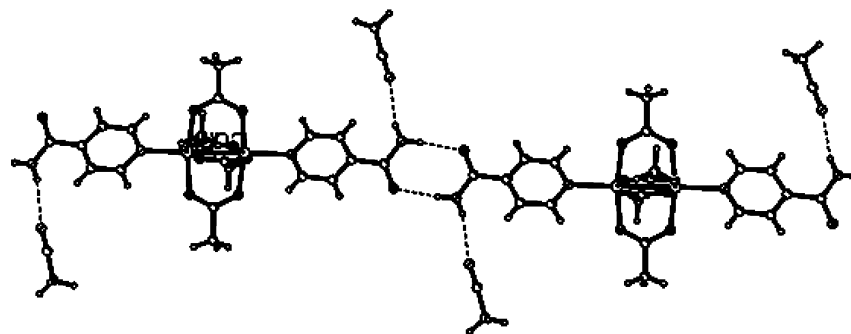


Fig. 2 Infinite chain of dinuclear Cu(II)-complexes in 1 held together by self-complementary amide...amide hydrogen-bond interactions.

Discussion

The crystal structures of 1–5 demonstrate that a specific intermolecular connector can be combined with very different (chemically and structurally) building blocks and still create a family of inorganic–organic hybrid materials that all display the same principal supramolecular connectivity. This observation is also reflected by the fact that the principal amide...amide hydrogen-bond interaction carries the same graph-set

description, $R_2^2(8)$ for all five structures. More importantly, this consistency (which can be equated with a high supramolecular synthetic ‘yield’) has been achieved in the presence of several potentially disruptive (in a structural sense) molecules, *e.g.* water, methanol, and acetic acid. For this set of compounds, the most consistent structural element is the self-complementary amide...amide interaction, which acts as a reliable linker between neighboring Cu(II) complexes even though they display dramatically different coordination geometries. A consequence

Table 3 Hydrogen-bond geometries for 1–5^a

	D–H	H ⋯ A	D ⋯ A	∠ (DHA)		
1	0.79(3)	2.29(3)	3.069(3)	166(3)	N7–H7A ⋯ N1S	
	0.84(3)	2.05(3)	2.881(2)	173(3)	N7–H7B ⋯ O7	$-x, -y + 1, -z$
2	0.83(3)	1.97(3)	2.794(3)	171(3)	O1S–H1S ⋯ O18	
	0.92(3)	1.85(3)	2.757(3)	167(3)	O1S–H2S ⋯ O18	$-x + 2, -y + 1, -z + 1$
	0.83(3)	2.33(3)	3.145(3)	170(3)	N7–H7A ⋯ O1S	$-x + 1, -y + 2, -z + 1$
	0.71(3)	2.19(3)	2.905(3)	175(3)	N7–H7B ⋯ O7	$3 - x + 1, -y + 3, -z$
3	0.86(3)	2.08(3)	2.930(3)	172(3)	N7–H7A ⋯ O27	$x + 1, y + 1, z - 1$
	0.86(3)	2.04(3)	2.879(3)	165(3)	N7–H7B ⋯ O32	$-x + 1, -y + 2, -z + 1$
	0.79(3)	2.11(3)	2.901(3)	174(3)	N27–H27A ⋯ O7	$x - 1, y - 1, z + 1$
	0.83(3)	2.11(3)	2.881(3)	154(3)	N27–H27B ⋯ O1S	$x, y - 1, z$
	0.83	1.95	2.754(3)	162.2	O1S–H1S ⋯ O42	
4	0.87(3)	1.99(3)	2.860(3)	176(2)	N17–H17A ⋯ O27	$x - 1, y, z - 1$
	0.89(3)	2.00(3)	2.875(2)	169(3)	N17–H17B ⋯ O42	$x, -y + 3/2, z - 1/2$
	0.74(3)	2.20(3)	2.940(3)	173(3)	N27–H27A ⋯ O17	$x + 1, y, z + 1$
	0.84(3)	2.14(3)	2.920(2)	154(2)	N27–H27B ⋯ O41	$x, -y + 3/2, z + 1/2$
	0.83	1.82	2.649(2)	173.0	O61–H61 ⋯ O32	
	0.83	1.81	2.634(3)	170.4	O51–H51 ⋯ O31	
5	0.76	2.16	2.891(3)	162.9	N17–H17A ⋯ O27	$x + 1, y, z + 1$
	0.65	2.25	2.889(3)	165.4	N17–H17B ⋯ O57	$x, -y + 1/2, z + 1/2$
	0.76	2.16	2.912(3)	170.3	N27–H27A ⋯ O17	$x - 1, y, z - 1$
	0.69	2.30	2.968(3)	164.5	N27–H27B ⋯ O58	$x, -y + 1/2, z - 1/2$

^a No suitable H-bond found for O38 ⋯ O47 = 2.568(3) Å.

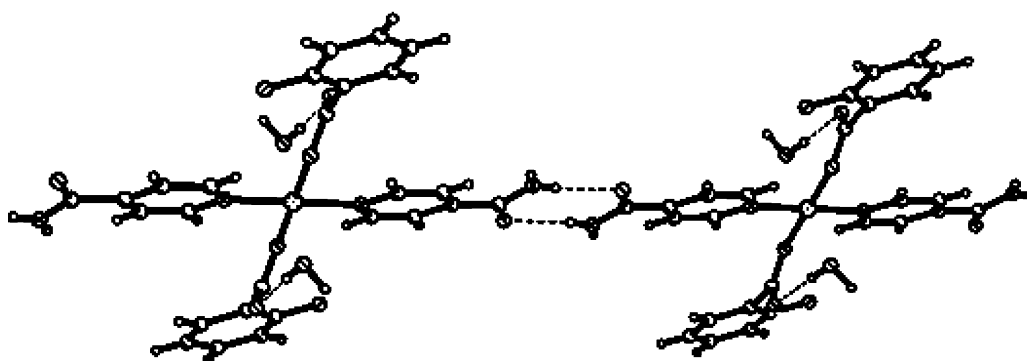


Fig. 3 Infinite chain of octahedrally coordinated Cu(II)-complexes in **2** held together by self-complementary amide ⋯ amide hydrogen-bond interactions.

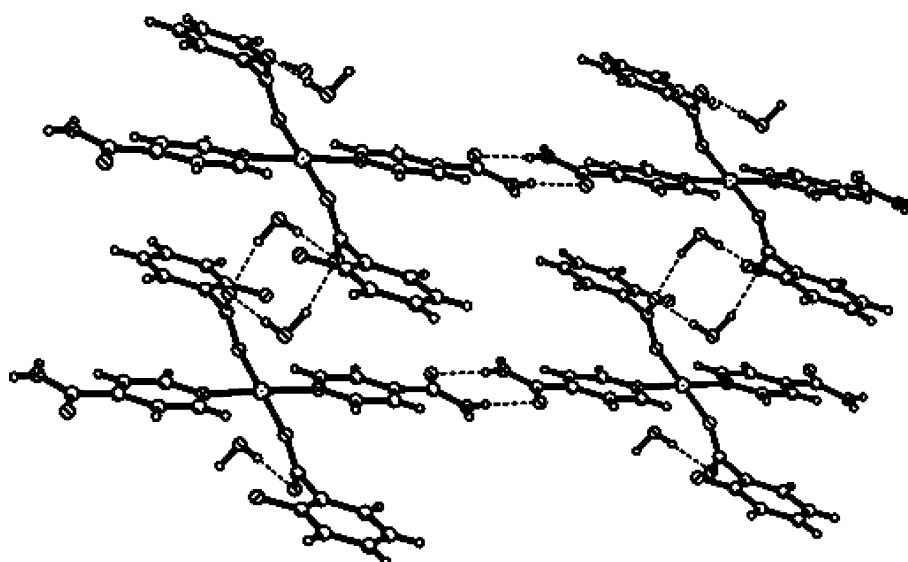


Fig. 4 Adjacent chains in **2** are bridged through hydrogen bonds involving coordinated water molecules.

of this supramolecular robustness is that the intra-chain separation of Cu(II) ions shows very little variation, 16.7–17.0 Å, despite large changes in the local environment around each

Cu(II) ion. This illustrates the fact that the very flexible and often unpredictable coordination chemistry of copper(II) does not, in itself, necessarily prevent subsequent successful

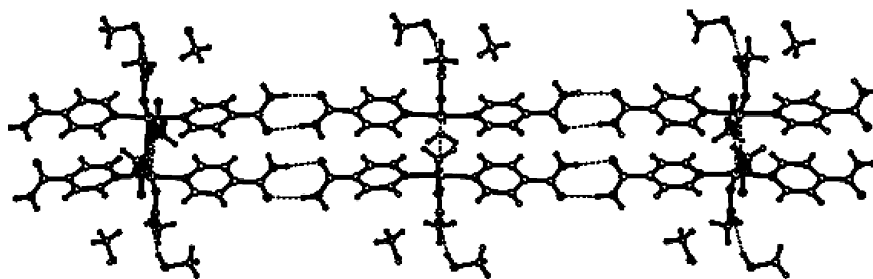


Fig. 5 Infinite chains of Cu(II)-complexes in **3** held together by self-complementary amide \cdots amide hydrogen-bond interactions.

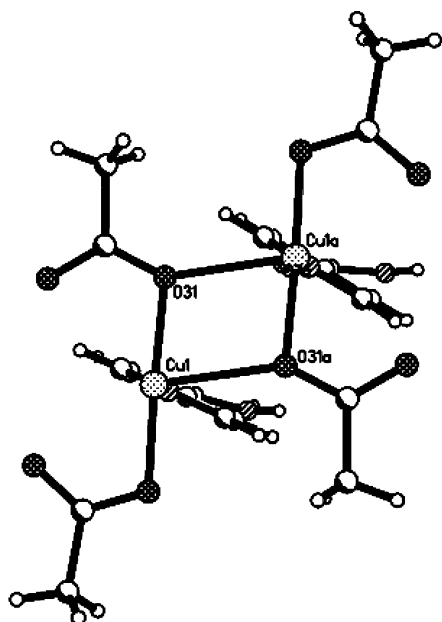


Fig. 6 The magnetic superexchange between neighbouring copper ions in **3** is most likely taking place through the μ -bridging oxygen atoms O31 and O31a.

supramolecular synthesis. Isonicotinamide appears to be a very effective supramolecular reagent for the construction of infinite 1-D metal-containing motifs.

The next phase in our investigation will employ a combination of reliable supramolecular reagents with coordination complexes where the coordination geometry is under stricter control with the aid of suitable chelating ligands.

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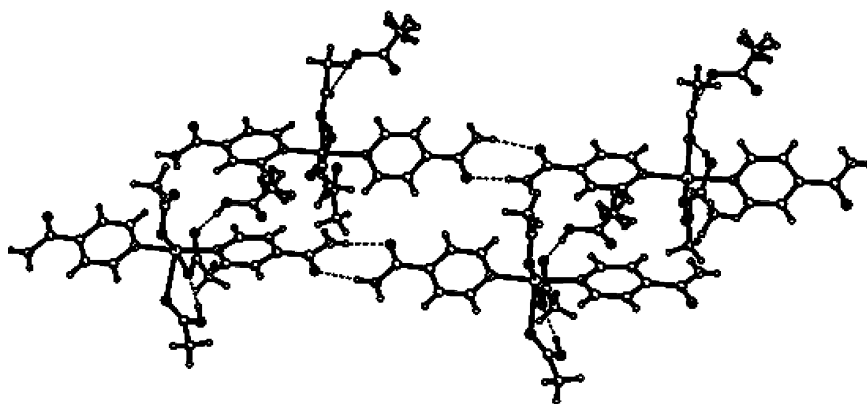


Fig. 7 Infinite chains of Cu(II)-complexes in **4** held together by self-complementary amide \cdots amide hydrogen-bond interactions and a charge assisted N–H \cdots O[−] interaction. Note that the chain remains intact even in the presence of two molecules of acetic acid in the lattice.

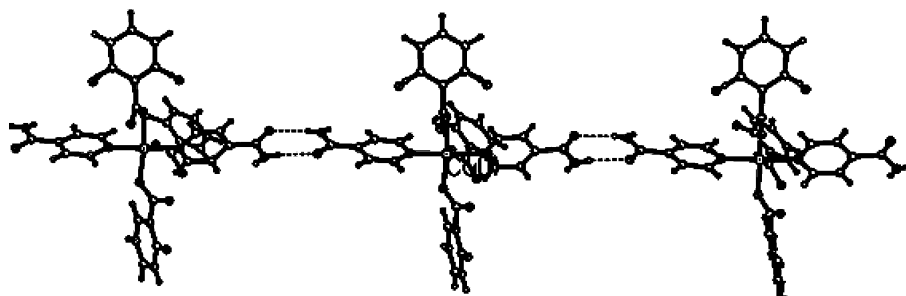


Fig. 8 Infinite chain of distorted square pyramidal Cu(II)-complexes in **5** held together by self-complementary amide \cdots amide hydrogen-bond interactions.

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