A crystalline hydrogen-bonded network with a poly-catenate topology†

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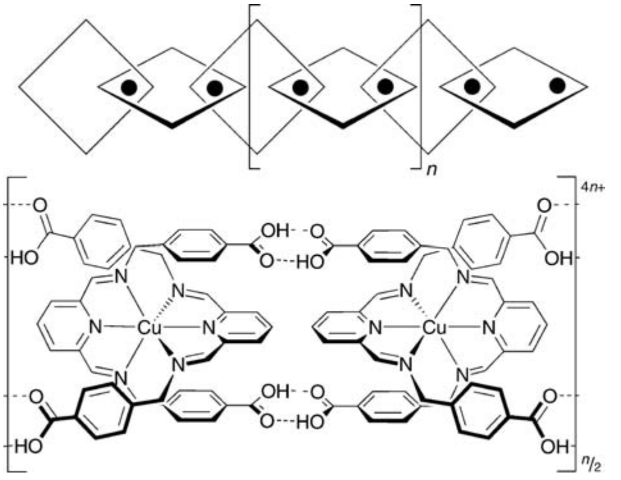
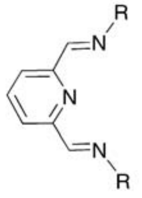
A polycatenate network, whose rings are formed from metal-templated hemispheres linked by hydrogen bonds, is reported.

Interlocked and threaded molecules like catenanes, catenates and rotaxanes are now well established.[1] They are prepared by ring-closing reactions of open-chain starting materials with appropriately functionalised side-arms, and/or by threading linear molecules through a pre-formed cyclic intermediate. The precursors in these reactions usually contain templating functionality, to orient the reagents in the correct fashion to yield the topological product.[2] Coordinative bonds to metal ions,[2–4] inter-arene π–π and charge-transfer interactions,[2,5] and hydrogen bonds,[2,6] are all commonly used for this purpose. Oligomeric and polymeric rotaxanes, containing one backbone threaded through multiple rings, are well established,[7,8] as are polymers of discrete [2]- or [3]-catenanes[7,9] or daisy-chain dimers[10] linked by linear spacers. However, no polymeric compound composed purely of interlocked rings (Scheme 1) has yet been properly characterised;[7,9,11] the longest that has been structurally authenticated is an oligocatenane with seven interlocked rings.[12] We report here a metal complex, **1**·1/2H_2O, that forms a hydrogen-bonded network with that topology. The rings in this [∞]-catenate structure are formed from strongly hydrogen-bonded carboxylic acid dimers, and are linked together by metal ion templates (Scheme 1). Metal ions bound to 2,6-di(carbaldimino)pyridine centres, like those in **1**, have been used previously by Leigh and Stoddart to template covalent catenates, rotaxanes and molecular knots.[3,13–15]

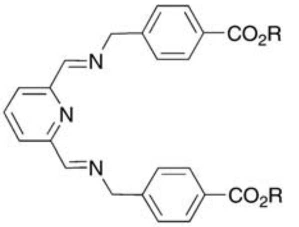
Our interest in $[Cu(L^R)]^{2+}$ compounds stems from their electronic structures, which depend on the identity of 'R'.[16] Most $[Cu(L^R)]^{2+}$ compounds adopt a $\{d_{y^2-z^2}\}^1$ electron configuration,‡ giving rise to a pseudo-Jahn–Teller structural elongation along one of the two N{imine}–Cu–N{imine} directions in the molecule.[17–19] However, when R is sterically bulky (R = *t*Bu)[17] or strongly electron-withdrawing (R = NH_2 or OH),[20] the copper ion switches to a $\{d_{z^2}\}^1$ d-orbital occupancy, with a structural compression along the unique N{pyridine}–Cu–N{pyridine} axis. This change in structure can be hard to detect crystallographically, because of disorder phenomena, but is easily recognised by EPR spectroscopy.[16]



Scheme 1 Structure of an [∞]-catenate (● = a metal ion), and the [∞]-catenate network structure of the dication in **1**·1/2H_2O.



L^R



R = H, L^1
R = CH_3, L^2

Reaction of pyridine-2,6-dicarbaldehyde, 4-(aminomethyl)-benzoic acid and hydrated $Cu[BF_4]_2$ in a 2 : 4 : 1 molar ratio at 298 K, in a 1 : 6 MeOH : CF_3CH_2OH solvent mixture, affords a green precipitate. This is insoluble in all organic solvents, but small amounts can be dissolved in aqueous NaOH. Such solutions at pH 9 slowly deposit lime-green crystals of $[Cu(L^1)_2][BF_4]_2$·1/2H_2O (**1**·1/2H_2O).§¶ The asymmetric unit of **1**·1/2H_2O contains half a formula unit, with a six-coordinate copper ion Cu(1) spanning a crystallographic C_2 axis (Fig. 1). The unique Cu–N{imine} bonds [Cu(1)–N(9) = 2.247(2) and Cu(1)–N(21) = 2.292(2) Å] are substantially longer than the Cu–N{pyridine} bond [Cu(1)–N(2) = 1.984(2) Å]. This distribution of bond lengths might reflect a pseudo-Jahn–Teller elongation disordered over the N(9)–Cu(1)–N(21) and N(9^i)–Cu(1)–N(21^i) directions, or a structural compression along the N(2)–Cu(1)–N(2^i) axis (symmetry code i: 1 − *x*, *y*, 3/2 − *z*).[16] A TLS analysis[21] of the structure supported the latter suggestion, in that all the Cu–N bonds exhibit $\langle d^2 \rangle \leq 63 \times 10^4$ Å^2 (ESI;†a disordered Jahn–Teller

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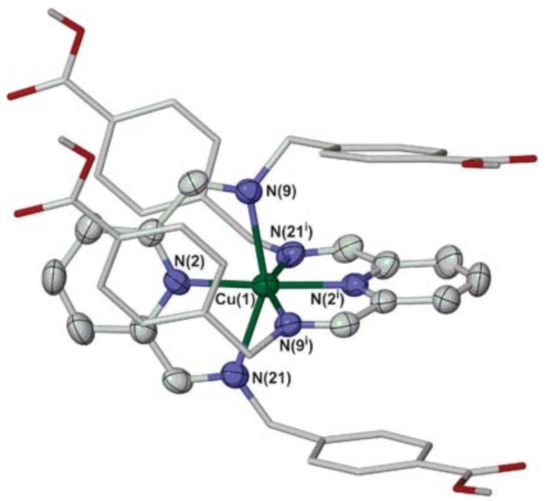

Fig. 1 View of the complex cation in **1**·1/2H_2O. All C-bound H atoms have been omitted for clarity. Thermal ellipsoids are at the 50% probability level except for the 4-carboxyphenylmethyl substituents, which have arbitrary radii. Symmetry code i: $1 - x$, y, $3/2 - z$.

elongation axis usually affords $\langle d^2\rangle > 100 \times 10^4$ Å^2 for the affected Cu–N bonds[16,20]). EPR data from the compound are inconsistent with that interpretation, however (see below).

The phenylcarboxy arms of the unique L^1 ligand are almost co-parallel, and sandwich the pyridyl ring of the other ligand in the molecule (Fig. 1). The carboxy groups of neighbouring molecules, related by $1/2 - x$, $1/2 - y$, $1 - z$, dimerise through the common cyclic $R_2^2(8)$ hydrogen-bonding motif.[22] This affords centrosymmetric rings of L^1 hemispheres linked by two pairs of O–H···O hydrogen bonds. The rings in turn are interlocked *via* the coordinated copper ions, affording polymeric chains of $(L^1)_2$ rings zig-zagging along the crystallographic [101] direction. The rings contain free space, with interior dimensions of 3.9 × 4.5 Å. This is occupied by the disordered BF_4^- anions, with one F atom protruding into each side of the rings, and by a weak Fourier peak near the centre of the rings that was modelled as a 25%-occupied water molecule (ESI†). There are two symmetry-related water sites in each ring, so half the rings in the polymer have a water molecule occupying one of two positions within them, while the other half do not (Fig. 2). The partial water molecule forms a close contact to one pyridyl C–H group, and is positioned to hydrogen bond to one of the ring carboxy groups, and/or to both neighbouring BF_4^- ions (ESI†).

The compound $[Cu(L^2)_2][BF_4]_2$ (**2**) was also synthesised by an analogous reaction using methyl 4-(aminomethyl)benzoate as starting material.§ Complex **2** is sterically similar to **1**, but lacks any hydrogen-bonding capability. The ligand conformation and Cu–N distances in crystals of **2**·CH_3NO_2 are similar to those in **1**·1/2H_2O.¶ However, unlike **1**, a TLS analysis of **2** implied the presence of masked disorder in the metal coordination sphere, since one of the two unique Cu–N{imine} bonds showed a high $\langle d^2\rangle$ value of 123(13) × 10^4 Å^2 (ESI†). That suggests this compound adopts a $\{d_{y^2-z^2}\}^1$ ground state with a pseudo-Jahn–Teller elongation, that is disordered over the two N{imine}–Cu–N{imine} axes in the molecule.‡

The X-band EPR spectra of solid **1**·1/2H_2O and **2** at 113–114 K are broad but have apparently axial lineshapes, with a $g_\parallel > g_\perp > 2.0023$ pattern and resolved $A_\parallel\{^{63,65}Cu\}$ hyperfine coupling (ESI†). The g and $A_\parallel$ values of the compounds at this temperature are essentially identical, and comparable to those of other $[Cu(L^R)_2]^{2+}$ complexes with a $\{d_{y^2-z^2}\}^1$ electron configuration.‡[17,18] That is the expected electronic structure for a $[Cu(L^R)_2]^{2+}$ compound without sterically bulky R substituents.[17–19] These data are consistent with the TLS analysis from the crystal structure of **2**, which clearly implied the presence of a disordered axis of elongation about its copper ion, but not of **1**. The anomalous rigidity of the coordination sphere of **1**·1/2H_2O, implied by its lower $\langle d^2\rangle$ values, might be a consequence of the catenate structure. That could be expected to make the conformation of L^1 more rigid, particularly given the occupancy of the catenate rings by anions and (partially) by water. Be that as it may, formation of the catenate network from $[Cu(L^R)_2]^{2+}$ centres clearly does not trigger gross changes in their electronic structure.

Samples of **1**·1/2H_2O lose their crystallinity when dried *in vacuo*, giving a green powder analysing as anhydrous **1**.§ A thermogravimetric analysis (TGA) of pre-dried **1** showed a gradual mass loss of 3.6% between *ca.* 50 and 150 °C (ESI†). Annealing **1** at 170 °C *in vacuo* for 6 h afforded a brown material **3**. Peaks attributable to the water molecule, that are present in the IR spectrum of **1**·1/2H_2O, are missing from the spectrum of **3**, but there are no other significant differences

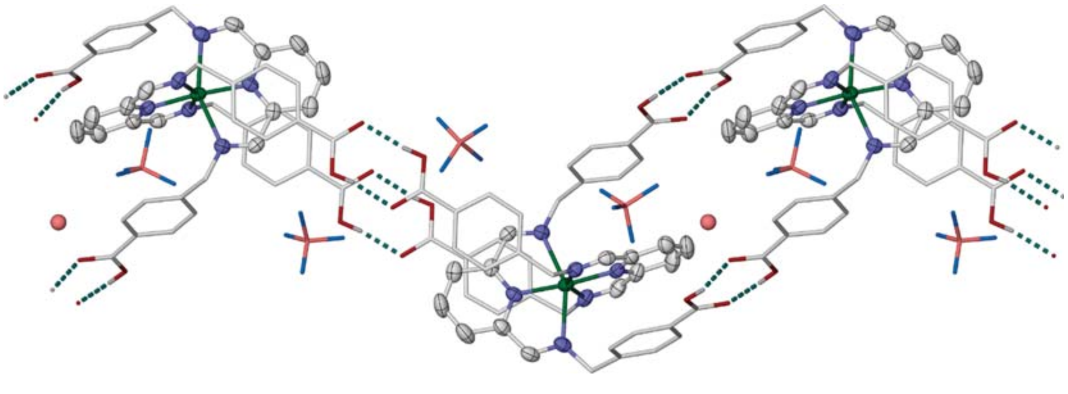

Fig. 2 View of the 1-D polymeric network structure of **1**·1/2H_2O. Only the major orientation of the disordered BF_4^- anions is shown. Occupancy of one of the two partial water sites in half of the ring cavities is shown. Thermal ellipsoids are at the 50% probability level except for the 4-carboxyphenylmethyl substituents, BF_4^- ions and water sites which have arbitrary radii.

between the two IR spectra (ESI†). In particular, the L^1 $\nu\{C{=}O\}$ stretch occurs at 1693 cm^{-1} in **1**·1/2H_2O and 1692 cm^{-1} in **3**. That strongly implies the thermal decomposition product **3** has retained its catenate network structure. The EPR spectrum of **3** at 120 K is identical to that of **1**·1/2H_2O around this temperature, implying that the ligand environments about the copper(II) centres in the two compounds are the same. Elemental microanalysis of **3** showed an increase in C, H and N compared to **1**, and could be fit by the formula $[Cu(L^1)_2][BF_4]_{1.4}$.§ We therefore conclude that the thermal decomposition of **1** to **3** has no effect on the L^1 ligands, but involves reduction of a fraction of the copper centres to copper(I) with concomitant loss of BF_4^- (presumably as BF_3 and HF and/or F_2[23]). That would be consistent with the brown colour of **3**, since some $[Cu(L^R)_2]^{2+}$ complexes are known to undergo reduction to dark brown $[Cu(L^R)_2]^+$ under mild conditions.[17] The discrepancy between the inorganic mass loss from **1** predicted by the microanalysis of **3** (5.0%) and that observed by TGA (3.6%), might be a consequence of the long annealing time used to form **3**. That could have allowed the reduction of **1** to proceed to a greater extent than in the TGA experiment.

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Notes and references

‡ A $\{d_{y^2-z^2}\}^1$ configuration is equivalent to the more familiar $\{d_{x^2-y^2}\}^1$. The $\{d_{y^2-z^2}\}^1$ nomenclature reflects the fact that a (pseudo)-Jahn–Teller elongation in $[Cu(L^R)]^{2+}$ does not lie on the unique symmetry axis of the molecule.[16]

§ Elemental microanalyses. For **1**·1/2H_2O: found C, 52.5; H, 4.0; N, 7.7%. Calcd for $C_{46}H_{39}B_2CuF_8N_6O_{8.5}$ C, 52.7; H, 3.8; N, 8.0%. For anhydrous **1**: found C, 53.3; H, 3.9; N 8.0%. Calcd for $C_{46}H_{38}B_2CuF_8N_6O_8$ C, 53.1; H, 3.7; N, 8.1%. For **2**: found C, 54.8; H, 4.2; N, 7.8%. Calcd for $C_{50}H_{46}B_2CuF_8N_6O_8$ C, 54.8; H, 4.2; N, 7.7%. For **3**: found C, 56.1; H, 3.9; N 8.3%. Calcd for $C_{46}H_{38}B_{1.4}CuF_{5.6}N_6O_8$ C, 55.9; H, 3.9; N, 8.5%.

¶ *Crystal data for* **1**·1/2H_2O, M_r = 1048.99, monoclinic, $C2/c$, a = 18.2288(13), b = 10.6790(7), c = 25.053(2) Å, β = 108.035(4)°, V = 4637.3(6) $Å^3$, Z = 4, T = 150 K, $\mu(\text{Mo-K}_\alpha)$ = 0.565 mm^{-1}, 35 938 measured reflections, 6000 independent, R_{int} = 0.037; $R_1(I > 2\sigma(I))$ = 0.062, wR_2(all data) = 0.185. The asymmetric unit contains half a complex dication with Cu(1) lying on the C_2 axis [1/2, y, 3/4]; and one BF_4^- anion lying on a general position. An additional Fourier peak that was not bonded to any other atom was also included, as a 1/4-occupied water molecule. The BF_4^- ion is disordered over three sites with occupancies of 0.5, 0.3 and 0.2, with the latter two sharing a common half-occupied B atom. The B–F bonds were restrained to the refined value of 1.38(2) Å, and the F···F distances in each partial anion site to 2.25(2) Å. All wholly occupied non-H atoms and the major anion disorder site were refined anisotropically, while all H atoms were placed in calculated positions and refined using a riding model. The carboxylic acid H atoms were not located in the Fourier map, and their placement in the model on O(19) and O(31) is arbitrary. In practise these H atoms are likely to be disordered over the two O atoms in each carboxy group. CCDC 692204. *Crystal data for* **2**·CH_3NO_2, M_r = 1157.13, trigonal, $P3_121$, a = 10.6124(15), c = 39.273(8) Å, V = 3830.5(11) $Å^3$, Z = 3, T = 150 K, $\mu(\text{Mo-K}_\alpha)$ = 0.524 mm^1, 48 423 measured reflections, 6787 independent, R_{int} = 0.032; $R_1(I > 2\sigma(I))$, wR_2(all data) = 0.137, Flack parameter = 0.010(14). The asymmetric unit contains half a complex dication, with Cu(1) lying on the C_2 axis [0, y, 1/6]; one BF_4^- ion lying on a general position; and half a molecule of nitromethane spanning the C_2 axis [x, x, 0]. The BF_4^- anion is disordered over three equally occupied sites. All B–F bonds were restrained to the refined value of 1.39(2) Å, and F···F distances within each partial anion to 2.27(2) Å. All wholly occupied non-H atoms, plus the half-occupied non-H atoms in the solvent molecule, were refined anisotropically. All H atoms were placed in calculated positions and refined using a riding model. A figure and a table of metric parameters for this structure are given in the ESI†. CCDC 692205.

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