Generation of an equilibrating collection of circular inorganic copper(I) architectures and solid-state stabilisation of the dicopper helicate component

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Cu^I ions and ligand L self-assemble to generate in solution a mixture of the double helical 1, triangular 2 and square grid 3 complexes, from which 1 has been crystallized and its crystal structure determined.

Within the field of supramolecular inorganic chemistry, self-assembly provides direct access to complex architectures comprising spatially and geometrically well defined arrays of metal ions.[1,2] Widely diverse morphologies have been obtained, such as helicates,[1,2c] pseudorotaxane racks,[3] ladders,[4] grids,[5] rings[6] and cages.[7] In order to design species presenting specific structural and functional features, it is of great importance to establish the rules by which control of the self-assembly process can be achieved through chemical programming by means of suitable components and assembling algorithms. Mixtures of ligands and metal ions that combine preferentially into one out of a range of possible self-assembled species provide an opportunity for studying how ligand design and choice of metal ion can influence the product distribution and thus the self-assembly pathway.[6,8]

On the other hand, mixtures of ligands and metal ions may yield mixtures of complexes resulting from the reversible combination of the different constituents. Such a situation represents a process of dynamic combinatorial chemistry (DCC) of inorganic supramolecular type, making potentially available a wide variety of combinations representing the members of a virtual combinatorial library (VCL).[6a,b,9] Of special interest is then the possibility to select and express a given member of the VCL for specific purposes, for instance by means of external factors. In the inorganic domain, such behaviour has been observed in the assembly of circular helicates.[6a,b]

We present here a case where a mixture of a ligand and of metal ions yields in solution a collection of self-assembled species, from which a single product can be isolated in the solid state by appropriate adjustment of the conditions.

When nitromethane was added to a 1 : 1 mixture of ligand L† and $[Cu(MeCN)_4]PF_6$ and the mixture stirred at ambient temperature under argon for 24 h, a dark brown–orange colour rapidly developed indicative of the coordination of Cu^I to L. Removal of solvent under vacuum yielded a dark brown solid which upon analysis by electrospray mass spectrometry showed clearly the formation of the oligomeric complexes $[Cu_nL_n]^{n+}$ (n = 2, 3, 4) as the dominant species present at 1×10^{-4} mol dm^{-3} in CH_2Cl_2.‡ The ^1H NMR spectrum of the product in CD_2Cl_2 consisted of a complicated pattern of sharp peaks characteristic of an equilibrium mixture of slowly exchanging species. Detailed analysis of the data (^1H–^1H COSY measurements) indicated the presence of three major species in proportions roughly equal to 6 : 4 : 3 for **1**, **2** and **3**, respectively. In addition a minor compound was also present (*ca.* 5%); the relative amounts appeared to be insensitive to changes in concentration. In CD_3NO_2 solution, the spectrum simplified to give nine broad bands corresponding to ligand L in a single chemical environment and indicative of medium-fast exchange between different copper(I) containing entities. In CD_3CN solution, the peaks sharpened indicating rapid equilibration of the species on the NMR timescale.

When a nitromethane solution of the above reaction mixture was layered with benzene and left to stand, all the material present crystallised as large dark brown blocks. A crystal structure determination§ showed that the product was the binuclear complex **1** composed of two ligands L wrapped in a helical arrangement around two Cu^I ions separated by 7.579 Å (Fig. 1). Both ligands are seen to be curved when viewed perpendicular to their mean planes and have therefore to adopt a strained conformation in order to coordinate both Cu^I ions. There are four intramolecular stacking interactions (within 3.5 Å) between each phenyl ring and a terminal pyridine ring of the partner ligand. The coordination polyhedron about each Cu^I ion is highly distorted and intermediate between tetrahedral and square-planar geometries, with Cu–N bond lengths of 2.017(9)–2.132(9) Å and N–Cu–N angles of 75.9(4)–78.8(4)° (chelate ring) and 110.9(4)–144.6(4)° (interligand). In addition, the crystals were found to be homochiral, so that the complex has undergone spontaneous resolution upon crystallisation.

Redissolution of the crystals in CD_2Cl_2 results in instant regeneration of a ^1H NMR spectrum identical to that of the crude reaction mixture prior to crystal growth as described above, showing that complex **1** rapidly opens in solution to form an equilibrium mixture of products. The proportions of each species and the preferential crystallisation of only **1** result from an interplay of enthalpic, entropic and crystal packing factors.

On the basis of the structure of **1** as well as of the spectrometric data, the other two substances present in solution may be considered to be the triangular complex **2** and the square [2 × 2] grid type structure **3** (Scheme 1).

In conclusion, a 1 : 1 combination of L with Cu^I generates in solution an equilibrating mixture of the self-assembled inorganic architectures **1**, **2** and **3**, which converts into the single species **1** in the solid state upon crystallisation. These features represent an attractive illustration of a dynamic combinatorial chemistry process, yielding an inorganic supramolecular library of complexes from which a single member may be trapped by crystallisation. The latter result is also of interest with respect to

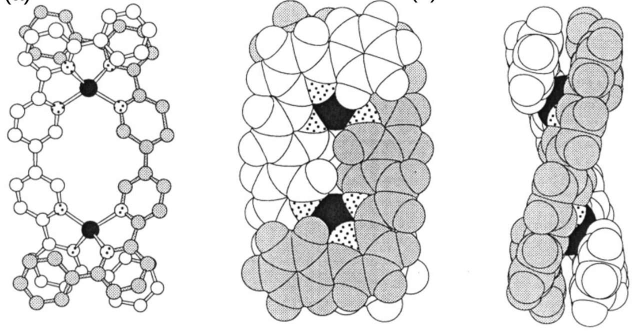
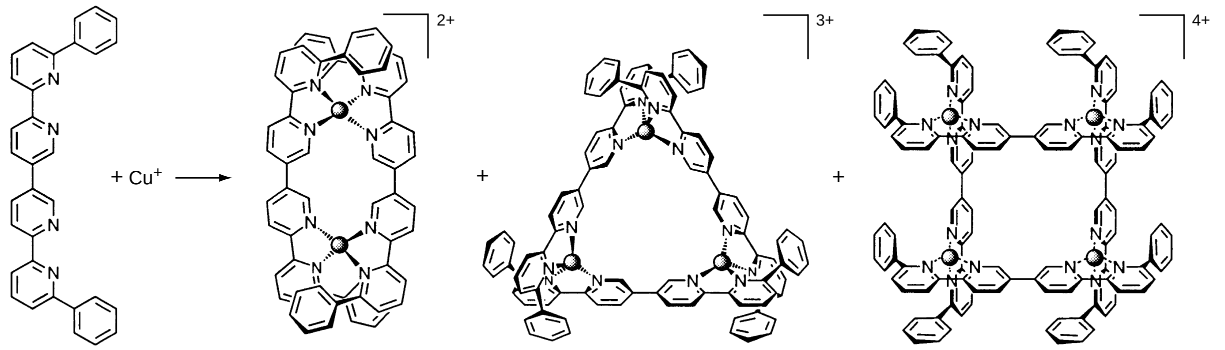


Fig. 1 Crystal structure of the double-helical complex **1**; (*a*) ball-and-stick, (*b*) space-filling representations



L 1 2 3

Scheme 1 Self-assembly of an equilibrating mixture of the double-helical **1**, triangular **2** and square [2 × 2] grid **3** complexes from L and Cu^I. Complexes **2** and **3** can in principle exist in different interwoven structures; only one structure is shown here.

crystal engineering and the investigation of the factors that dictate solid state selection processes.

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Footnotes

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† Ligand L was prepared following the same synthetic route as the analog bearing methyl groups in place of the phenyl groups.[5b]

‡ ESMS (10^{-4} mol dm^{-3} CH_2Cl_2) *m/z* (rel. intensity %); 1868 (2) $\{[Cu_3L_3](PF_6)_2\}^+$, 1196.8 (5) $\{[Cu_2L_2]PF_6\}^+$, $\{[Cu_4L_4](PF_6)_2\}^{2+}$, 861.5 (82) $\{[Cu_3L_3]PF_6\}^{2+}$, 749.8 (12) $\{[Cu_4L_4]PF_6\}^{3+}$, 526.2 (100) $[Cu_2L_2]^{2+}$, $[Cu_3L_3]^{3+}$, $[Cu_4L_4]^{4+}$. Very weak peaks are also present, which could correspond to the minor species observed in the NMR spectrum. Microanal. Calc. for $C_{32}H_{22}CuF_6N_4P$, $\{CuLPF_6\}$: C, 57.27; H, 3.30; N 8.35. Found C, 57.32; H 3.29; N 8.57%.

§ *Crystal data* for **1**: $C_{64}H_{44}Cu_2F_{12}N_8P_2\cdot 2C_3H_6O\cdot C_6H_6$, M_r = 1536.36, monoclinic, space group *Cc*, a = 30.374(1), b = 8.092(1), c = 34.132(3) Å, β = 123.15(1)°, U = 7023(1) Å^3, Z = 4, D_c = 1.453 Mg m^{-3}, $F(000)$ = 3144, T = 293 ± 1 K, crystal dimensions 0.3 × 0.4 × 0.4 mm, dark red–brown, 4703 collected reflections, of which 4226 unique (R_{int} = 0.027) were recorded on an Enraf-Nonius CAD4 diffractometer using graphite monochromatised Mo-Kα radiation (λ = 0.7017 Å) and ω–2θ scan mode (scan width ° 0.65 × 0.35 tanθ) to 2θ = 45° (h $0 \rightarrow 32$, k $0 \rightarrow 8$ and l $-36 \rightarrow 36$). L_p correction, absorption correction based on ψ-scans was applied [max., min. abs. corr. 1.44 and 1.16, respectively, μ(Mo-Kα) = 0.737 mm^{-1}]. The structure was solved by direct methods (SHELXS)[10] and subjected to full-matrix least-squares refinement (SHELXL)[11] on F_o^2. All non-H atoms were refined anisotropically. The H-atoms were calculated in idealised positions and refined as riding atoms with fixed isotropic temperature factors. Eight geometrical restraints were used to keep feasible geometry for the solvent molecules. Final R indices: [$I > 2\sigma(I)$] R_1 = 0.0537, wR_2 = 0.1386; (all data) R_1 = 0.0711, wR_2 = 0.1518 for 907 parameters. Owing to the acentric space group a Flack's absolute structure parameter was refined to 0.03(2). Goodness-of-fit on F_o^2 = 1.099. Convergence max. shift/error < 0.01, largest diff. peak and hole 0.539 and -0.352 e Å^{-3}. Atomic coordinates, bond lengths, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/501.

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