

Inorganic arrays *via* multicomponent self-assembly: the spontaneous generation of ladder architectures

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Self-assembly of the linear oligobipyridine ligands **3 or **4**, of the bipyrimidine **5** and of copper(I) ions generates the inorganic architectures of ladder type **1** or **2**.**

A major line of development of supramolecular chemistry lies in the spontaneous generation of well defined architectures by self-assembly from suitably designed components and selected interactions.^{1,2} This is the case for inorganic superstructures that self-assemble from ligand components of appropriate structure by interconnection through metal ions of given coordination geometry. In this category, a rich variety of inorganic architectures such as helicates,^{1,3–5} rings,⁶ cages,⁷ grids⁸ and rotaxanes⁹ have been generated from polybipyridine ligand systems and transition-metal ions.

Structures of this type result from the operation of defined structural and interactional instructions. They may display a range of novel physicochemical properties not expressed by their isolated component parts such as new redox, magnetic, optical and catalytic functions of interest in particular for materials science. The key feature is the ability to generate in a controlled fashion arrays of ligands and metal ions of well defined geometries. Among these, linear arrays of $[n]$ -rack type¹⁰ and two-dimensional arrays of $[m \times n]$ -grid type^{8a} have been reported recently by our group. The intermediate case is represented by structures of ladder type, $[2 \times n]L$.

We herein present evidence for the formation of such 2×2 (**1**) and 2×3 (**2**) ladder complexes (Fig. 1), which form upon combination of the oligobipyridine ligands **3**⁷ or **4**, the bipyrimidine **5**¹¹ and Cu^I ions in a 2:2:4 and 2:3:6 stoichiometry of **3**:**5**:Cu^I and **4**:**5**:Cu^I respectively.

To a mixture of **3**⁷ (0.030 g, 8.86×10^{-5} mol), **5**¹¹ (0.041 g, 8.86×10^{-5} mol) and $[Cu(MeCN)_4]PF_6$ (0.066 g, 1.77×10^{-4} mol) under argon, was added MeNO₂ (5 ml) *via* a syringe, and the resulting brown mixture stirred at ambient temperature for 168 h. All suspended solids went into solution. The solvent was then removed under vacuum and the product purified by chromatography on Geduran silica, eluting first with 2% MeOH–CH₂Cl₂ and then with 5% MeOH–CH₂Cl₂ to remove the product. Final purification was achieved upon recrystallisation by the dropwise addition of toluene to a concentrated MeNO₂ solution, isolation by vacuum filtration, washing with toluene and drying at 65 °C (2×10^{-6} mm Hg) to yield 0.065 g (60%) of **1** as dark brown needles. Complex **2** was prepared in a similar way from a mixture of 0.030 g (6.09×10^{-5} mol) of **4**,¹² 0.042 g (9.08×10^{-5} mol) of **5**, and 0.068 g (1.82×10^{-4} mol) of $[Cu(MeCN)_4]PF_6$ in 5 ml MeNO₂ under argon. Work-up using conditions similar to those above (except for product elution with 7% MeOH–CH₂Cl₂), yielded 0.066 g (60%) of **2** as dark brown needles.

The structures of complexes **1** and **2** (space filling representation shown in Fig. 2) were unambiguously assigned on the basis of ¹H and ¹³C NMR and electrospray mass spectrometric (ESMS) evidence. The ¹H NMR spectra of the reaction products were strikingly simple and indicative of the presence of a single highly symmetric species in both cases. A more detailed inspection of the NMR data (including ¹H–¹H COSY and ROESY experiments) strongly suggested that the identity of the species present corresponded to the proposed tetra- and hexanuclear ladder type architectures **1** and **2** (Fig. 1). For example in the spectrum assigned to structure **2**, the *ortho* and *meta*

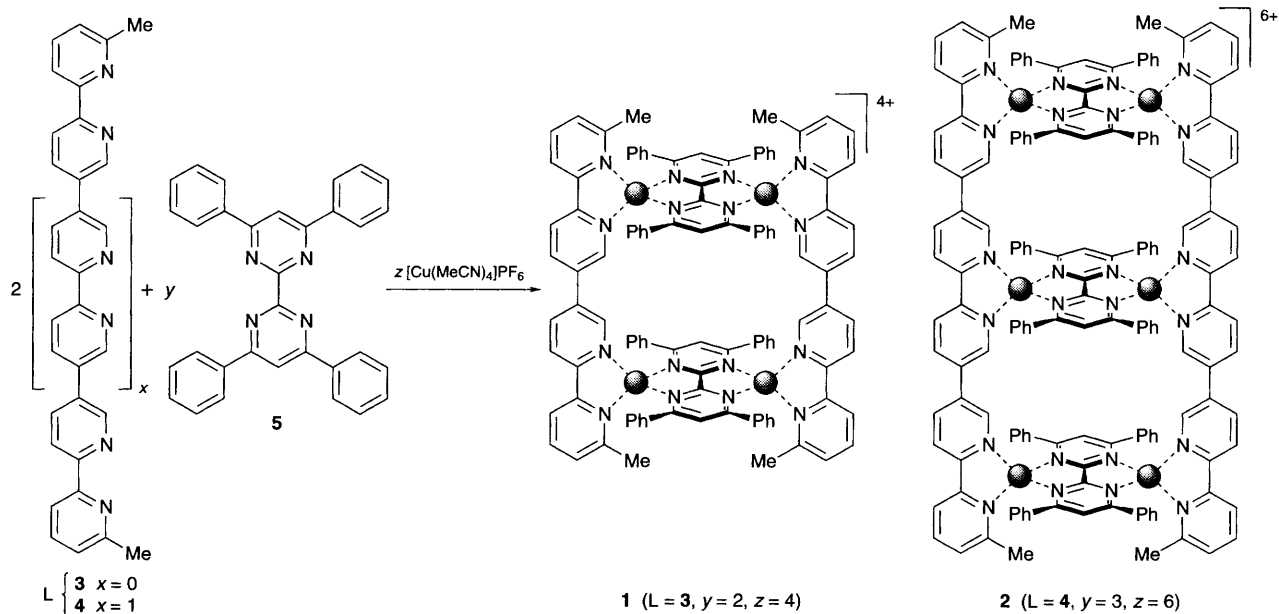


Fig. 1 Self-assembly of two- and three-rung ladders, the tetranuclear $[2 \times 2]L$ (**1**) and hexanuclear $[2 \times 3]L$ (**2**) complexes

phenyl ring protons of ligand **5** are each divided into two groups in a ratio of 2 : 1 which correspond with the two outer and single inner **5** ligands ('rungs') of the ladder. Similarly proton **5** of the pyrimidine rings of ligand **5** appears in two different environments again in a 2 : 1 ratio indicative of the outer and inner ligands **5**. Furthermore, the *ortho* and *meta* phenyl ring protons and the protons of the pyrimidine rings of the ligand **5** assigned to the inner position, are substantially shielded with respect to those assigned to the outer ligands **5**, as expected for ligand protons situated within the interior of such a structure. The *para* phenyl ring protons of the outer and inner ligands **5** should be much less susceptible to shielding effects as they are located on the exterior of the complex cation and point away from its outer surface. Indeed, they are found not to be split into two groups but to have the same chemical shift. Interestingly, the 3, 4 and 5 protons of the terminal pyridine rings of ligands **3** and **4** appear to be in a single environment and are well separated (upfield) from the remaining interior pyridine ring protons. This has also been observed in the ¹H NMR spectra of a structurally related and crystallographically characterised hexanuclear copper(I) cage complex.⁷ In the case of the spectrum assigned to structure **2**, this suggests that the ligands **4** are in identical magnetic and chemical environments and therefore have a parallel rather than staggered relationship to each other, further supporting the above conclusions. The ¹³C NMR spectra of the products from the above two reactions displayed respectively 18 and 30 signals, as expected for structures **1** and **2**.

The UV–VIS electronic spectra of the above reaction products also agreed with structures **1** and **2**. The spectrum of the product from the reaction between **5** and [Cu(MeCN)₄PF₆] in a 1 : 1 stoichiometric ratio in 1% MeCN–CH₂Cl₂ displayed bands at 408 and 541 nm. The spectrum of a 1 : 1 combination of **3** and [Cu(MeCN)₄]PF₆ in 5% MeCN–CH₂Cl₂ showed only one absorption at 472 nm. On the other hand, all the above bands were absent in the spectra of the reaction products, which instead consisted of two bands centred at *ca.* 427 and 569 nm. This implies that entities incorporating mixed ligand [Cu(5L)]⁺ (L = **3**, **4**) chromophores such as **1** and **2** were the dominant species present in the solutions. Also, the ratio of the reaction product absorption coefficients was found to be the expected 1 : 1.5 when calculated for structures **1** and **2**.

ESMS measurements provided final unequivocal evidence for the assignment of structures **1** and **2** to the above reaction products. The ES mass spectrum of the product from [4Cu^I + 2(**3**) + 2(**5**)] showed three bands at *m/z* 667 (100), 1073 (30) and 2293 (1%), corresponding to the cationic species {[Cu₄3₂5₂](PF₆)₃}³⁺, {[Cu₄3₂5₂](PF₆)₂}²⁺ and

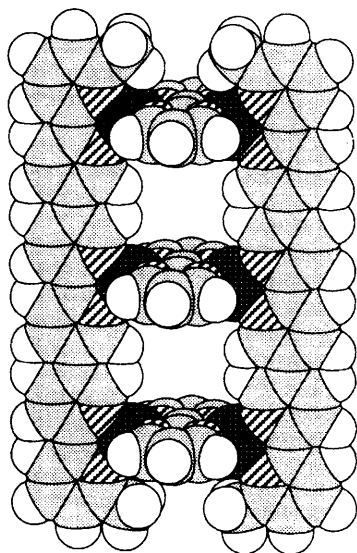


Fig. 2 Computer-generated (MM2) space-filling representation of the [2 × 3]L ladder type complex **2** (bipyrimidine phenyl rings omitted for clarity)

{[Cu₄3₂5₂](PF₆)₃}⁺ respectively. The spectrum of the product from [6Cu^I + 2(**4**) + 3(**5**)] displayed only three bands, *i.e.* at *m/z* 761 (100), 1063 (58) and 1667 (3%) due to the ions {[Cu₆4₂5₃](PF₆)₂}⁴⁺, {[Cu₆4₂5₃](PF₆)₃}³⁺ and {[Cu₆4₂5₃](PF₆)₄}²⁺ respectively. The cationic species observed in both of the above spectra could therefore only have derived from the ladder type architectures **1** and **2**. No further counter-ion loss from the highest charged ions was observed. Lastly, the mass spectra of both complexes (recorded at 10⁻⁴–10⁻³ mol dm⁻³ in CH₂Cl₂) were free of peaks corresponding to dissociation products, showing that the complexes were stable to dilution at least down to the millimolar concentration range.

In conclusion, the present results allow the assignment of the tetranuclear (2 × 2)L (**1**) and hexanuclear (2 × 3)L (**2**) ladder-type architectures to the products from the reaction between 2(**3**) : 2(**5**) : 4Cu⁺ and 2(**4**) : 3(**5**) : 6Cu⁺. Complexes **1** and **2** form by the self-assembly of eight and eleven particles respectively upon combination of Cu⁺ ions and ligands in the correct stoichiometric ratio. The self-assembly occurs through the operation of a programmed system¹ in three main stages; (a) recognition between the constituent particles, (b) growth by progressive interconnection of components and finally (c) termination leading to a discrete supramolecular entity. In addition, **1** and **2** are generated from a mixture of two different ligand species, through a process representing a mixed-ligand self-assembly, which extends further the structural and informational complexity achievable in metal-ion constructed supramolecular architectures. Future developments may for instance concern the precise two-dimensional ordering of metal ions on surfaces and the construction of three-dimensional metal ion arrays.

The ladders **1** and **2** represent the first oligomeric members of a new class of spatially well defined 2 × *n* (*n* > 2) arrays of metal ions which can be spontaneously generated without the need for laborious sequential microfabrication steps. This feature makes such systems attractive candidates as components in a future molecular electronic information processing nanotechnology accessible through self-assembly.¹

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