

# Self-assembly of a symmetric tetracopper box-grid with guest trapping in the solid state

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**Reaction of ligand 2 with Cu<sup>I</sup> ions leads to the self-assembly of the distorted [2 × 2] grid complex 1 of box-like shape, featuring a well defined cavity and trapping of guest molecules.**

The controlled generation of molecular entities that contain geometrically precisely defined arrangements of metal ions is of considerable current interest within the fields of supramolecular chemistry and materials science.<sup>1</sup> The presence of metal ions in such coordination arrays may result in the development of many varied physicochemical properties such as electrochemical, optical, magnetic, mechanical and catalytic activity for example.

Metal ion-directed self-assembly currently provides a very efficient method of access to coordination arrays of predetermined nuclearity and spatial composition<sup>2</sup> such as helicates,<sup>3</sup> pseudorotaxane racks,<sup>4</sup> grids,<sup>5,6</sup> rings<sup>7</sup> and cages.<sup>8</sup> The inorganic grids represent a particularly intriguing class of coordination arrays which may potentially function as components of systems such as molecular memory devices, in which information might be stored in the form of electron holes or occupancies at specific sites or areas within the architecture.

With ligands presenting a greater spatial separation between the metal ion binding sites than previously reported,<sup>5,6</sup> a cavity of controlled dimensions would be opened up within the grid structure. Such a cavity may exhibit selective guest inclusion, which if combined with redox activity of the grid itself, may result in a class of electrochemical guest sensors. Towards this goal, the linear ditopic tetradentate ligand **2** was constructed. A grid composed of four **2** ligands and four metal ions of tetrahedral coordination geometry should possess an internal box-shaped cavity lined by aromatic rings, of suitable dimensions for the inclusion of small molecules.

We herein report the structural characterisation and some physicochemical features of the self-assembled symmetric [2 × 2]G tetracopper grid (**1**) which is generated from **2**<sup>†</sup> and copper(I) ions; it is electrochemically active and exhibits guest inclusion in the solid state.

The tetracopper grid **1** forms in almost quantitative yield<sup>‡</sup> in nitromethane solution upon admixture of a 1 : 1 stoichiometric ratio of the linear ligand **2** and [Cu(MeCN)<sub>4</sub>PF<sub>6</sub>]. The structure of **1** both in solution and in the solid state has been established on the basis of <sup>1</sup>H and <sup>13</sup>C NMR, FAB and ES mass spectroscopy, microanalysis and X-ray crystallography.

The <sup>1</sup>H NMR spectrum<sup>‡</sup> of the above reaction product in nitromethane solution consisted of a very simple pattern of peaks corresponding to ligand **2** in a single magnetic and chemical environment, and suggestive of the formation of a highly symmetrical species. The <sup>13</sup>C spectrum also consisted of the expected fifteen peaks.

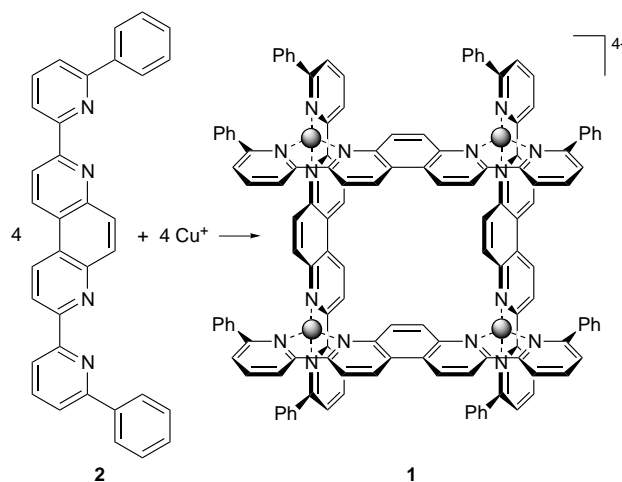
FAB and ES mass spectroscopy were found to be especially informative in identifying the above reaction product as **1**. The highest *m/z* peaks observed in the FAB mass spectrum, were assignable to the tetracopper grid **1** with successive loss of PF<sub>6</sub><sup>-</sup> counter ions, *i.e.* 2635.2 {[Cu<sub>4</sub>(**2**)<sub>4</sub>](PF<sub>6</sub>)<sub>3</sub>}<sup>+</sup>, 2490.2 {[Cu<sub>4</sub>(**2**)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub>}<sup>+</sup> and 2345.3 {[Cu<sub>4</sub>(**2**)<sub>4</sub>](PF<sub>6</sub>)<sup>+</sup>. Peaks at

lower *m/z* ratios corresponded to mono- and di-nuclear species which arise through fragmentation/dissociation of **1**. The EMS peaks (recorded at 10<sup>-4</sup> in MeNO<sub>2</sub>) of the reaction product at *m/z* 1245.3, 781.9 and 550.3 were assignable to the species {[Cu<sub>4</sub>(**2**)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub>}<sup>2+</sup>, {[Cu<sub>4</sub>(**2**)<sub>4</sub>](PF<sub>6</sub>)<sub>3</sub>}<sup>3+</sup> and [Cu<sub>4</sub>(**2**)<sub>4</sub>]<sup>4+</sup>, respectively. Upon dilution to 10<sup>-6</sup> M, the peaks corresponding to counter ion loss from **1** decrease in intensity and peaks which arise from the dissociation of **1** increase in height showing that **1** undergoes dissociation at high dilution.

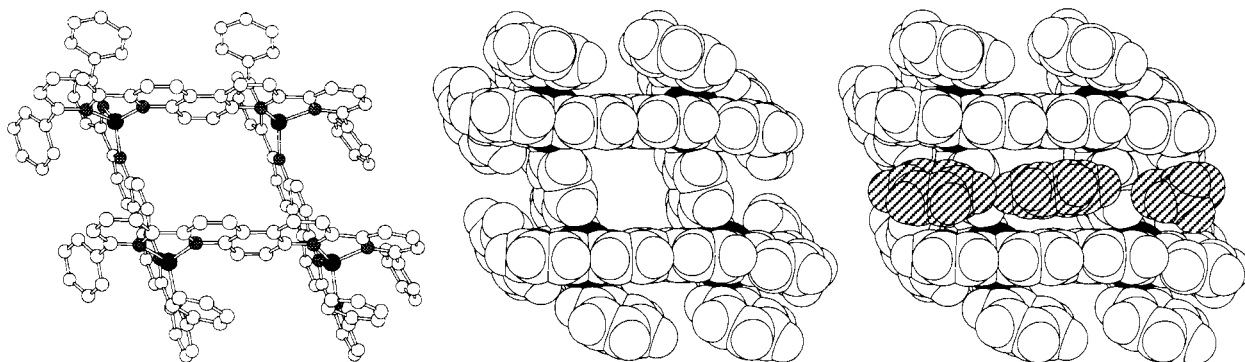
An X-ray crystal structural analysis finally provided unambiguous evidence that the identity of the above reaction product was that of **1**.§ The cation is indeed a tetranuclear distorted square grid composed of four copper(I) ions and four **2** ligands, with overall external dimensions (including van der Waals radii) of 22.5 × 15.4 × 12.5 Å (depth). The ligands are divided into two parallel pairs, one of which lies above and the other below the mean plane through the four copper ions. The grid is not a square but a rhombus (inner angles, *i.e.* angles between the mean planes of **2** of 74.5 and 105.5°) owing to deviation from perfect tetrahedral coordination geometry about each metal centre, with the ligands forming the sides and the copper(I) ions (7.7 Å apart) lying at the corners. The Cu–N bond lengths, 2.055–2.002 Å and N–Cu–N angles are unexceptional. The complex cation possesses an internal box-shaped void of area 4.2 × 3.8 Å and 12.5 Å depth.<sup>9</sup> Six guests, four benzenes and two nitromethane molecules are trapped in the grooves defined by the parallel pairs of the ligands, with a benzene lying in the mouth of the cavity on each side of the cation (Fig. 1).

Cyclic voltammetric measurements showed **1** to be electrochemically active, giving a single reversible oxidation wave at 0.44 V, and three closely spaced reversible reduction waves at –1.56, –1.65 and –1.79 V (vs. Fc/Fc<sup>+</sup>).¶

The [2 × 2]G symmetric tetracopper grid **1** forms by the self-assembly of eight articles, four metal ions and four ligand components. It exhibits multiple guest inclusion in its box-



Scheme 1 Self-assembly of the inorganic [2 × 2] box-grid **1**



**Fig. 1** Crystal structure of the grid-type complex **1**; ball and stick representation (left); space-filling representation (centre); space-filling representation of **1** with guests in upper groove (right); guests in lower groove omitted for clarity

shaped cavity in the solid state. The presence of the phenyl rings on the ligands appears to be essential for its formation. If the phenyl rings of **2** are replaced by H or Me groups, then 1 : 1 mixtures with  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  under identical conditions to the formation of **1** yield oligomeric mixtures and insoluble coordination polymers as the only products.

In addition to their possible use as components of molecular electronics devices, inorganic grids capable of trapping guest species may be of potential interest for chemical catalysis and selective guest sensing. They could therefore find various applications in materials science and nanotechnology.

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## Footnotes and References

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† Ligand **2** was prepared from 2-trimethylstannyl-6-phenylpyridine and 3,8-dibromo-4,7-phenanthroline via a Stille coupling protocol.

‡ *Experimental*: to a mixture of 0.030 g ( $6.17 \times 10^{-5}$  mol) of **2** and 0.023 g ( $6.17 \times 10^{-5}$  mol) of  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  under an atmosphere of argon was added 4 ml of  $\text{MeNO}_2$  via syringe, and the dark-brown solution stirred at ambient temperature for 48 h. All solvent was then removed under vacuum and the remaining solid purified by gel permeation chromatography on a column of SX-1 biobeads using nitrobenzene as eluent. The product was collected in one fraction, reduced in volume to 3 ml under vacuum at 70 °C and precipitated by the addition of an excess of toluene. The solid was collected by filtration under vacuum, washed with toluene, recrystallised twice from  $\text{MeNO}_2$ -toluene and finally dried under vacuum at 90 °C/2 × 10<sup>-6</sup> mmHg. The above work-up yielded 0.039 g (91%) of the product complex **1** ( $\text{PF}_6$ )<sub>4</sub> as a dark-brown microcrystalline solid. <sup>1</sup>H NMR spectral assignments were made on the basis of <sup>1</sup>H–<sup>1</sup>H COSY and ROESY measurements.

**1** ( $\text{PF}_6$ )<sub>4</sub>: <sup>1</sup>H NMR ( $\text{CD}_3\text{NO}_2$ , 500 MHz, 25 °C),  $\delta$  9.39 [d, 8 H, H(2-1',10),  $J_{1'2/10'9'}$  8.9 Hz], 8.59 [d, 8 H, H(2-2',9'),  $J_{2'1'9'10'}$  9.0 Hz], 8.31 [d, 8 H, H(2-3,3''),  $J_{3,4/3'',4}$  8.0 Hz], 8.10 [t, 16 H, H(2-4,4''),  $J_{4,3/4,5; 4'',3''/4'',5''}$  7.8 Hz], 7.70 [s, 8 H, H(2-5',6''), 7.63 [d, 8 H, H(2-5,5''),  $J_{5,4/5'',4''}$  7.5 Hz], 7.06 [d, 16 H, H(2-ortho),  $J_{0,m}$  7.3 Hz], 6.99 [t, 8 H, H(2-para),  $J_{p,m}$  7.4 Hz], 6.60 [t, 16 H, H(2-meta),  $J_{m,o/m,p}$  7.5 Hz]. <sup>13</sup>C NMR ( $\text{CD}_3\text{NO}_2$ , 75 MHz, 25 °C),  $\delta$  159.92, 154.72, 153.04, 145.75, 140.50, 140.15, 134.93, 133.39, 130.37, 128.72, 128.43, 127.60, 127.31, 123.23, 122.15. FABMS,  $m/z$  (rel. intensity %): 2635.2 (4.3)  $[\{\text{Cu}_4(\mathbf{2})_4\}(\text{PF}_6)_3]^+$ , 2490.2 (2.1)  $[\{\text{Cu}_4(\mathbf{2})_4\}(\text{PF}_6)_2]^+$ , 2345.3 (0.3)  $[\{\text{Cu}_4(\mathbf{2})_4\}(\text{PF}_6)]^+$ , 1245.1 (6.6)  $[\{\text{Cu}_2(\mathbf{2})_2\}(\text{PF}_6)^{2+}]$ , 1173.1 (2.3)  $[\{\text{Cu}_4(\mathbf{2})_4\}(\text{PF}_6)^{2+}]$ , 1035.9 (7.6)  $\{\text{Cu}(\mathbf{2})\}^+$ , 549.5 (100)  $\{\text{Cu}(\mathbf{2})\}^+$ . ESMS ( $10^{-4}$  M  $\text{MeNO}_2$ ),  $m/z$  (rel. intensity %): 1245.3 (3.2)  $[\{\text{Cu}_4(\mathbf{2})_4\}(\text{PF}_6)_2]^{2+}$ , 944.1 (19.0)  $[\{\text{Cu}_4(\mathbf{2})_5\}(\text{PF}_6)]^{3+}$ , 781.9 (59.7)  $[\{\text{Cu}_4(\mathbf{2})_4\}(\text{PF}_6)]^{3+}$ , 671.9 (39.6)  $[\text{Cu}_4(\mathbf{2})_5]^{4+}$ , 550.3 (100)  $[\text{Cu}_4(\mathbf{2})_4]^{4+}$ . UV–VIS ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda/\text{nm}$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 593 (6391), 482 (14 164), 341 (118 331), 259 (83 672). Microanal. (Calc. for  $\text{C}_{136}\text{H}_{88}\text{Cu}_4\text{F}_{24}\text{N}_{16}\text{P}_4$ , C, 58.75; H, 3.19; N, 8.06. Found: C, 58.83; H, 3.41; N, 8.10%.

§ *Crystal data* for  $[\{\text{Cu}_4(\mathbf{2})_4\}(\text{PF}_6)_4 \cdot 10\text{C}_6\text{H}_6 \cdot 4\text{CH}_3\text{NO}_2]$ : Brown blocks grown by benzene diffusion into nitromethane solution. Crystal size = 0.1

× 0.1 × 0.2 mm. STOE.IPDS diffractometer (−80 °C), graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.710 73 \text{ \AA}$ ), monoclinic, space group  $C2/c$ ,  $a = 24.782(5)$ ,  $b = 26.645(5)$ ,  $c = 29.101(6) \text{ \AA}$ ,  $\beta = 110.02(3)^\circ$ ,  $U = 18055(6) \text{ \AA}^3$ ,  $Z = 8$ ,  $D_c = 1.400 \text{ Mg m}^{-3}$ ,  $\mu = 0.590 \text{ mm}^{-1}$ ,  $F(000) = 7824$ ,  $M = 1902.76$ ,  $2\theta_{\text{max}} = 52^\circ$ . Primary structure solution by direct methods (SHELXS-92).<sup>10</sup> Anisotropic refinement for all non-hydrogen atoms (SHELXL-93).<sup>11</sup> The structure was refined against  $F^2$  (full-matrix least squares). The final weighting scheme was  $w^{-1} = \sigma^2(F_o^2) + (0.0776P)^2 + 12.3113P$ , with  $P = (F_o^2 + 2F_c^2)/3$ ,  $R_1 = 0.0503$  ( $F > 4\sigma F$ ) and  $wR_2 = 0.1487$  (all data), GOF on  $F^2 = S = 1.041$ , max. min. residual density: +0.458, −0.401 e  $\text{\AA}^{-3}$ , ( $R_1 = \sum | |F_o| - |F_c| | / \sum |F_o|$ ,  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$ , GOF =  $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ , where  $n =$  no. of reflections and  $p =$  no. of parameters). CCDC 182/649.

¶ Electrochemical measurements were performed under argon in  $\text{CH}_2\text{Cl}_2$  with 0.1 M  $[\text{NBU}^n_4]\text{ClO}_4$  (oxidation) and  $[\text{NBU}^n_4]\text{PF}_6$  (reduction) as the supporting electrolytes.

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