

Self-assembled metal–organic squares derived from linear templates as exemplified by a polydentate ligand that provides access to both a polygon and polyhedron

Giannis S. Papaefstathiou, Tamara D. Hamilton, Tomislav Frišćić and Leonard R. MacGillivray*

Department of Chemistry, University of Iowa, Iowa City, IA, 52242-1294, USA.

E-mail: len-macgillivray@uiowa.edu; Fax: 319-335-1270; Tel: 319-335-3504

Received (in Columbia, MO, USA) 15th October 2003, Accepted 27th November 2003

First published as an Advance Article on the web 7th January 2004

Di- **1a** and tetranuclear **1b** metal–organic squares have been obtained from bis- and tetra(pyridyl)cyclobutanes synthesized in the solid state, respectively; for **1b**, a cyclobutane with two different metal binding subunits supports the formation of a polygon and polyhedron.

The prospect that establishing control of reactivity in the organic solid state can lead to the solvent-free synthesis of molecules,¹ and the development of functional solid-state materials,² continues to generate much interest and attract researchers into such a challenging area.³ In this context, we have recently described a supramolecular⁴ approach to control reactivity in the organic solid state that employs molecules, in the form of linear templates,⁵ to direct the [2+2] photodimerisation by way of hydrogen bonds. A major driving force behind employing linear templates to direct the solid-state reaction has been an ability to enforce the photoreaction to occur within discrete, hydrogen-bonded molecular assemblies with structures largely independent of structure effects of crystal packing, effects which have made the photoreaction difficult to control.³ Consequently, the photodimerisation can now be directed regioselectively and used to conduct molecular synthesis by design.⁵

In addition to controlling reactivity in solids, an attractive feature of employing linear templates to direct reactivity, in either solution or the solid state,⁶ is that the peripheries of the products are lined with convergent and/or divergent functional groups in the form of hydrogen bond donor and/or acceptor sites. Such groups, owing to their ubiquity in coordination- and hydrogen-bond-driven molecular self-assembly,⁷ make the products potential bi- and polyfunctional linkers of functional (*e.g.* catalysis) self-assembled frameworks. Such applications of products derived from linear templates, however, remain rare⁸ and promise, in addition to self-assembly,⁷ to contribute to advance linear templates⁶ and the organic solid state^{1,3} by enabling the templates to be used as tools to construct building units with unique, predetermined solid-state structures.

With this in mind, we wish to report here the design and formation of di- and tetranuclear metal–organic squares⁹ [Cu₂(4-pyr-4-Cl-p-cb)₂(hfacac)₄] (where: 4-pyr-4-Cl-p-cb = *rctt*-1,2-bis(4-pyridyl)-3,4-bis(4-chlorophenyl)cyclobutane; hfacac = hexafluoroacetylacetonate) **1a** and [Cu₄(2,4-tpcb)₂(hfacac)₈] (where: 2,4-tpcb = *rctt*-1,2-bis(2-pyridyl)-3,4-bis(4-pyridyl)cyclobutane) **1b**, respectively, derived from linear templates that operate in the solid state (Scheme 1). In the case of **1b**, the metal binding information written by the templates, as a tetradentate cyclobutane with two different metal binding subunits,¹⁰ has produced a polygon with a structure that complements a recently reported polyhedron^{8a} [Cu(2,4-tpcb)₆(H₂O)₆][X]₁₂ **2** (where X = ClO₄⁻, NO₃⁻) based on the same metal ion and photoproduct. To our knowledge, the ability of a polydentate ligand – a fundamental building unit of a polyhedron¹¹ – to provide access to both a polygon and polyhedron has not been reported and, consequently, represents a key step towards understanding structural factors that lie at the boundary between self-assembled polygonal¹² and polyhedral structures.¹³

To construct a metal–organic square using a molecule derived from a linear template, we anticipated that two cyclobutanes, each with two 4-pyridyl groups attached in a *cis* geometry, could provide

four edges and two approximate right angles of the polygon. In this design, two metal-based units could provide the two remaining corners to give a square with a dinuclear structure. In this context, we selected Cu(hfacac)₂ as a source of a 90° angle. Structure studies indicated that two chelating hfacac anions can adopt a *cis* geometry around a Cu(II) center,¹⁴ which could enable the 4-pyridyl units of the two cyclobutanes to adopt a *cis* coordination that gives two 90° angles.

When 4-pyr-4-Cl-p-cb, obtained in 100% yield using 4-ethylresorcinol as a template, and Cu(hfacac)₂·H₂O (1:1 ratio) in benzene was layered with hexane, green-blue crystals of **1a**-benzene formed within two days (yield: 70%). **1a**-benzene was characterized by X-ray diffraction† and IR spectroscopy.

Views of **1a** are shown in Fig. 1. The components have assembled to form a dinuclear complex, two of which lie in the

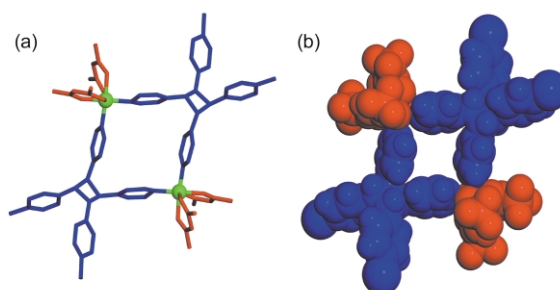
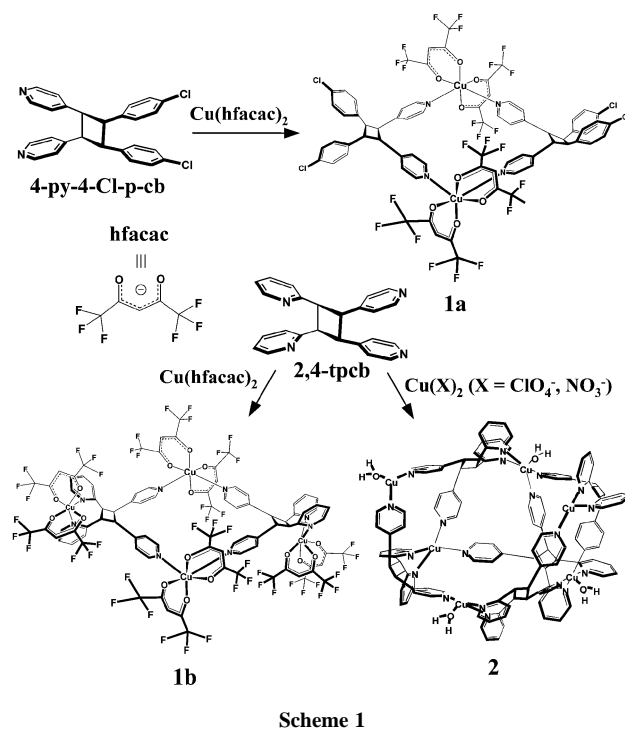


Fig. 1 Perspective of **1a**: (a) discrete assembly and (b) space-filling.

asymmetric unit and each of which sits around a crystallographic centre of inversion, with a topology that conforms to a square. Each Cu(II) ion adopts an octahedral coordination environment wherein two identical pyridines occupy *cis* positions and the remaining sites are occupied by two chelating hfacac ions. The 4-pyridyl units, which are twisted approximately orthogonal to the plane of the square, define the edges of each polygon while the two metal ions (Cu...Cu 9.1 Å) and two cyclobutane rings (cyclobutane...cyclobutane 11.0 Å) define opposite corners (Fig. 1a). As a consequence of the assembly process, squares with rhombus-shaped cavities, of dimensions approximately 4.0×4.3 Å (van der Waals radii) (Fig. 1b) and corner angles approximately 79° and 101° , have formed. The included benzenes are located between nearest-neighbour squares, being sandwiched between $-CF_3$ groups of coordinated hfacac anions.

We have also discovered that 2,4-tpcb with, in contrast to 4-pyr-4-Cl-p-cb, two different metal binding units gives a square. Specifically, when 2,4-tpcb, obtained in 100% yield using 4-chlororesorcinol as a template,^{8a} in $CHCl_3$ was added to a solution of $Cu(hfacac)_2 \cdot H_2O$ (1:2 ratio) in $CHCl_3$, a green solution resulted from which green-blue crystals of **1b**·3 $CHCl_3$ formed within one day (yield: 85%). **1b**·3 $CHCl_3$ was characterized by X-ray diffraction[†] and IR spectroscopy.

Views of **1b** are shown in Fig. 2. The components have assembled to form a tetranuclear complex, which sits around a crystallographic centre of inversion, with a topology that conforms to a square (Fig. 2a). Similar to **1a**, the cyclobutane serves as an angular bifunctional linker wherein each metal adopts an octahedral coordination environment with two identical *cis* pyridines and two chelating hfacac anions. In this arrangement, the 4-pyridyl units form the edges, which produce a dinuclear cavity (Cu(1)...Cu(1)a 9.2 Å) of dimensions approximately 4.0×4.2 Å (van der Waals radii) and corner angles of approximately 79° and 101° , while the 2-pyridyl groups serve as bifunctional chelators,^{8a} organizing the two remaining Cu(II) ions (Cu(2)...Cu(2)a 17.3 Å, Cu(2)...Cu(1) 9.3 Å, Cu(2)...Cu(1)a 10.3 Å) along the periphery of the complex (cyclobutane...cyclobutane 11.1 Å). These observations contrast **2** wherein 2,4-tpcb and the Cu(II) ion assemble to give a hexanuclear polyhedron, in the form of a trigonal antiprism,^{8a} with each metal in a square pyramidal coordination environment, the pyridyl groups of the trifunctional cyclobutane linker serving as *cis* bridges and bifunctional chelators. The square **1b** assembles to produce 1D arrays wherein the included $CHCl_3$ molecules interact with the anions *via* C–H...O forces (Fig. 2b).¹⁵

That a polydentate ligand can assemble with the same metal ion to form either a polygon or polyhedron is, to our knowledge, unique and can be attributed to structure-directing effects of the hfacac anions. As outlined by Stang,¹¹ a strategy that employs coordination-driven self-assembly with building units that define edges of polygons and polyhedra requires a bifunctional linker to form a polygon and at least one trifunctional linker to form a polyhedron. 2,4-tpcb meets both criteria by serving as a bi- and trifunctional linker in **1b** and **2**, respectively. Specifically, in the case of **1b**, the polydentate ligand is able to serve as a bifunctional linker owing to the ability of the chelating hfacac anions to limit the number of pyridyl units that bind to each Cu(II) centre to two. This means that each metal ion can accommodate either two chelating 2-pyridyl

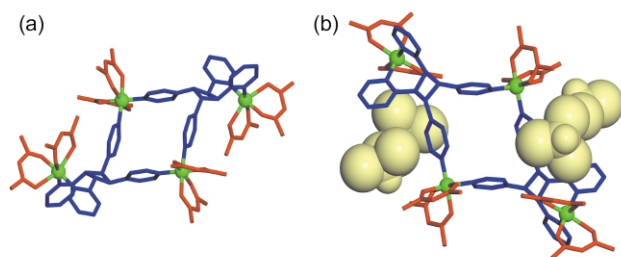


Fig. 2 Perspective of **1b**: (a) discrete assembly and (b) solvent inclusion.

units, from the same cyclobutane, or two bridging 4-pyridyl units, from different cyclobutanes, which, in a *cis* arrangement, form the edges of **1b**.§ This contrasts **2** wherein the bridging and chelating abilities of the cyclobutane occur, in the absence of a coordinating anion, at the same Cu(II) centre which, in turn, enables the cyclobutane to serve as a trifunctional linker, the 4-pyridyl units defining the edges of the polyhedron. In effect, the hfacac anions of **1b** have forced the binding information of the two different metal binding subunits to be expressed¹⁰ at different, rather than the same, metal centres. We believe that **1b** and **2** provide a distinctive case in which a polydentate ligand supports either a polygon or a polyhedron, and we are currently investigating whether such structure behaviour can be expressed dynamically in solution.¹⁰

In conclusion, metal–organic squares **1a** and **1b**, with hfacac anions as corners, have been derived from linear templates. For **1b**, a square that complements a polyhedron involving the same linker and metal has been realized. We believe these observations augur well for molecules derived from linear templates^{4–6} to serve as building units, or synthons,¹⁵ of coordination-driven self-assembled frameworks⁹ wherein **1b** represents an attractive illustration of a degree of structural complexity attainable by the approach. That 2,4-tpcb gives either a polygon or polyhedron may, for example, yield a system that exhibits anion-triggered guest release. We are exploring these, and related, host–guest properties.

We are grateful to the National Science Foundation (CAREER Award, L.R.M., DMR-0133138) and the University of Iowa for support of this work.

Notes and references

† Crystal data for **1a**·benzene: triclinic, space group $P\bar{1}$, $a = 14.904(3)$, $b = 17.547(4)$, $c = 17.836(4)$ Å, $\alpha = 119.46(3)$, $\beta = 97.41(3)$, $\gamma = 90.00(3)^\circ$, $U = 4017(1)$ Å³, $D_c = 1.568$ g cm⁻³, Mo K α radiation ($\lambda = 0.71070$ Å) for $Z = 2$ and $R = 0.055$.

‡ Crystal data for **1b**·3 $CHCl_3$: triclinic, space group $P\bar{1}$, $a = 10.844(5)$, $b = 16.351(5)$, $c = 17.738(5)$ Å, $\alpha = 69.309(5)^\circ$, $\beta = 83.259(5)$, $\gamma = 86.215(5)^\circ$, $U = 2921(2)$ Å³, $D_c = 1.704$ g cm⁻³, Mo K α radiation ($\lambda = 0.71070$ Å) for $Z = 1$ and $R = 0.057$.

§ The components of **1b** may, in principle, form a helix wherein the 4-pyridyl units lie a *cis* arrangement (see ref. 14)

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