

Discrete and infinite coordination arrays derived from a template-directed, solid-state, organic synthesis†

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Paper

A product derived from a template-directed, organic, solid-state synthesis, *rctt*-tetrakis(2-pyridyl)cyclobutane (2,2'-tpcb), serves as a bis-chelating ligand upon reaction with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to produce discrete and infinite coordination arrays, $[\text{Cu}_2(\text{NO}_3)_4(\mu\text{-}2,2'\text{-tpcb})]$ (**1**) and $[\text{Cu}_2(\mu_2\text{-SO}_4)_2(\mu\text{-}2,2'\text{-tpcb})(\text{H}_2\text{O})_2]_n \cdot 9\text{H}_2\text{O}$ (**2**), respectively.

Introduction

Reactions that occur in the solid state can produce molecules less available, or completely inaccessible, in the liquid phase.¹ With a suitable design, products of such reactions may, in principle, be engineered to exhibit properties not realised, or difficult to achieve, from solution. Despite this realisation, however, molecules derived from organic, solid-state reactions, save for selected industrial examples,² have encountered limited applications in synthetic chemistry, particularly in the context of routine laboratory synthesis. Such lack of use may be attributed to the difficulty in designing molecules, *a priori*, that crystallise in a necessary arrangement for reaction.¹ Indeed, subtle structure demands of weak intermolecular forces and crystal packing have hindered progress such that subtle changes to structures of reactants typically result, in contrast to solution, in a loss of solid-state reactivity.³ This has meant that chemists have remained largely unable to systematically study and apply molecules derived from the solid state to problems of chemical synthesis, a synthetic freedom virtually non-existent in solution.⁴

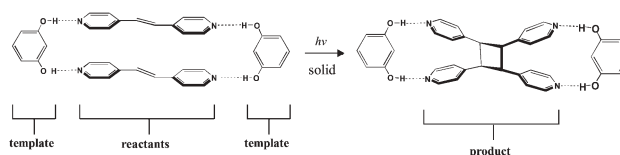
We have recently introduced a flexible method for controlling reactivity in the solid state.⁵ By using molecules in the form of linear templates⁶ largely preorganised to orient molecules, using hydrogen bonds, for $[2 + 2]$ photoreaction,⁷ we have demonstrated an ability to direct solid-state reactivity such that it is possible, similar to the liquid phase,⁴ to conduct a molecular synthesis by design. Co-crystallisation of 1,3-dihydroxybenzene (resorcinol) with *trans*-1,2-bis(4-pyridyl)ethylene (4,4'-bpe), for example, was shown to give a discrete four-component molecular assembly, 2(resorcinol)·2(4,4'-bpe), held together by four O–H···N hydrogen bonds wherein two double bonds are separated by < 4.2 Å and aligned parallel, a position suitable for a photoinduced $[2 + 2]$ cycloaddition reaction (Scheme 1).^{5a} Ultraviolet (UV) irradiation of the solid produced the desired photoproduct, *rctt*-tetrakis(4-pyridyl)cyclobutane, stereospecifically (yield 100%). Expansion of this method to two reaction centres, involving 5-methoxyresorcinol (5-OMe-res) as a template and 1,4-bis[2-(4-pyridyl)ethenyl]benzene (1,4-bpeb) as a reactant, was revealed to give an assembly, 2(5-OMe-res)·2(1,4-bpeb), that upon UV irradiation produced a targeted $[2,2]$ paracyclophane.^{5a}

An attractive feature of this template approach lies in the nature of the products. That hydrogen bond donors are used to organise the reactants means that each cyclobutane unit is lined with hydrogen bond acceptor sites in the form of pyridyl groups.⁶ Owing to the ubiquity of pyridyl groups in coordination chemistry,⁸ it occurred to us that such molecules may serve as useful ligands for the design of coordination complexes. That a bifunctional hydrogen bond donor is employed to direct the solid-state reaction would mean that the products must contain at least two pyridyl units. Moreover, this, in turn, may permit such molecules, owing to the divergent orientation adopted by the pyridyl groups along the cyclobutane ring, to serve as *exo*-dentate ligands. The ability of such products to behave as *exo*-dentate ligands could allow such molecules, for example, to function as novel building blocks for the design of supramolecular coordination arrays⁹ wherein the template dictates the structure of the ligand and resulting complex.

With this in mind, we report here the application of a product derived from a template-directed, solid-state, organic synthesis, in $[\text{Cu}_2(\text{NO}_3)_4(\mu\text{-}2,2'\text{-tpcb})]$ **1** and $[\text{Cu}_2(\mu_2\text{-SO}_4)_2(\mu\text{-}2,2'\text{-tpcb})(\text{H}_2\text{O})_2]_n \cdot 9\text{H}_2\text{O}$ **2** [where 2,2'-tpcb = *rctt*-tetrakis(2-pyridyl)cyclobutane], to the field of coordination chemistry. In the present cases, the assembly process gives rise to, in the case of **1**, a discrete and, in the case of **2**, an infinite one-dimensional (1D) coordination array wherein the product derived from the solid state serves as a hitherto unobserved bis-chelating ligand. Whereas 2,2'-tpcb forms in low yield, and as part of a mixture of products, in the liquid phase,¹⁰ that the tetrapyridine forms stereospecifically in quantitative yield in the crystalline state means that the template-directed synthesis has provided access to coordination complexes difficult to achieve from solution.

Experimental

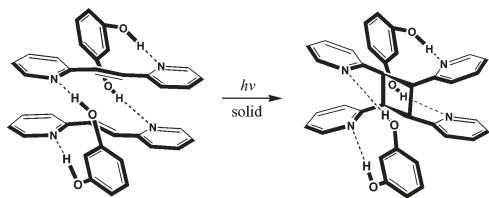
All reagents were purchased from Aldrich Chemical Co. and used as received unless otherwise stated.



Scheme 1

†Based on the presentation given at CrystEngComm Discussion, 29th June–1st July 2002, Bristol, UK.

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Scheme 2

Synthesis

***rctt*-Tetrakis(2-pyridyl)cyclobutane (2,2'-tpcb).** 2,2'-Tpcb was generated in quantitative yield in the solid state using a Hg lamp and resorcinol as a template (Scheme 2).^{5a} The irradiated solid was suspended in water and treated with NaOH until the suspension was basic to litmus. The photoproduct was then extracted with chloroform and recovered as a white solid using a rotary evaporator.

[Cu₂(NO₃)₄(μ-2,2'-tpcb)] (1). **1** was prepared by combining solutions of 2,2'-tpcb (0.025 g, 0.070 mmol) and Cu(NO₃)₂·2.5H₂O (0.032 g, 0.140 mmol) (1 : 2 ratio) in methanol (25 mL). To the resulting cloudy solution was added distilled water (5 mL). Single crystals of **1** were obtained by allowing the solution to evaporate to dryness for a period of approximately one week (yield 0.042g, 72%). IR, ν/cm⁻¹ (KBr pellets): 1607 (m), 1573 (w), 1492 (s), 1443 (w), 1384 (s).

[Cu₂(μ₂-SO₄)₂(μ-2,2'-tpcb)(H₂O)₂]_n·9H₂O (2). **2** was prepared according to the procedure described for **1** by combining solutions of 2,2'-tpcb (0.025 g, 0.070 mmol) and CuSO₄·5H₂O (0.034 g, 0.140 mmol) (1 : 2 ratio) in methanol (25 mL). Single crystals of **2** were obtained by allowing the solution to evaporate to dryness for a period of approximately one week (yield 0.038 g, 63%). IR, ν/cm⁻¹ (KBr pellets): 3435 (br), 1602 (m), 1572 (w), 1477 (s), 1438 (w), 1160 (w), 1108 (s), 1062 (w), 890 (w), 644 (w), 617 (s), 567 (w). The formulation of **2** was also confirmed by way of thermogravimetric analysis.

Crystal structure determination

Crystal data for **1** and **2** were measured using a Nonius Kappa CCD single-crystal X-ray diffractometer at 100 K. All crystallographic calculations were conducted using SHELXL-97¹¹ locally implemented on an IBM-compatible, pentium-based PC. Crystallographic information is summarised in Table 1.

Table 1 Crystal data for **1** and **2**^a

Parameter	1	2
Empirical formula	Cu ₂ C ₂₄ N ₈ O ₁₂ H ₂₀	Cu ₂ S ₂ C ₂₄ N ₄ O ₁₉ H ₄₂
Crystal dimensions/mm	0.05 × 0.11 × 0.15	0.20 × 0.20 × 0.50
<i>M</i>	739.59	881.86
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	9.542(2)	20.696(4)
<i>b</i> /Å	8.608(2)	9.425(2)
<i>c</i> /Å	17.139(3)	18.835(4)
β/°	90.30(3)	113.83(3)
<i>V</i> /Å ³	1408.0(5)	3360.7(12)
<i>Z</i>	2	4
<i>T</i> /°C	-100	-100
<i>D</i> _c /g cm ⁻³	1.75	1.74
μ/mm ⁻¹	1.56	0.818
No. unique reflections	1806	2179
No. reflections	1097	2096
[<i>I</i> > 2σ(<i>I</i>)]		
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0654	0.0240
<i>wR</i> ₂	0.1349	0.0651

^aClick here for full crystallographic data (CCDC 180743, 180744).

Spectroscopic and thermal studies

Infrared spectra were taken using a Perkin-Elmer FTIR spectrophotometer with ±1 cm⁻¹ resolution and scanned in the range 350–4000 cm⁻¹. The thermal analysis was conducted using a TA Instruments Hi-Res TGA 2950 thermal gravimetric analyser.

Results and discussion

A perspective of **1**, as well as selected interatomic distances, is given in Fig. 1. The metal and organic components have assembled to form a dinuclear complex, which sits around a crystallographic center of inversion. The coordination geometry of each metal may be regarded as a distorted octahedron involving two chelating NO₃⁻ ions¹² (O1, O2 and O4 and O5) and a 2,2'-tpcb ligand (N1 and N2). Owing to the positioning of the nitrogen atoms in the 2-position of each pyridyl group, the 2,2'-tpcb ligand, in a similar way to 1,2-bis(2-pyridyl)ethane,¹³ forms a boat-like, seven-membered chelate ring with each metal. The pyridyl groups of each chelating moiety, as defined by the centroids of the aromatic rings, are separated by 4.80 Å across the cyclobutane ring and are splayed at an angle of *ca.* 91.6° with respect to the metal centre. Thus the molecule derived from the solid-state synthesis serves as a tetrafunctional bis-chelating ligand wherein the two metal ions are, in effect, bridged by the cyclobutane unit (Cu···Cu separation 7.65 Å). To our knowledge, such chelating behaviour involving a cyclobutane ring has not been observed.

A view of the crystal structure of **1** is shown in Fig. 2. The complex organises in the solid state such that the nitrate ion based on N3 exhibits a 'tongue-and-groove' fit with the two splayed pyridyl rings of each chelating group [Fig. 2(a)]. This, in turn, gives rise to a 2D layered architecture within the crystallographic *bc*-plane [Fig. 2(b)]. Notably, C–H···O hydrogen bonds¹⁴ involving the nitrate ion and nearest-neighbour metal complexes have also formed [C···O separations: C3···O3 3.27(1), C4···O3 3.13(1) Å].

A perspective of **2**, as well as selected interatomic distances, is given in Fig. 3. As in the case of **1**, 2,2'-tpcb serves as a tetrafunctional bis-chelating ligand, the cyclobutane unit bridging two Cu centers (Cu···Cu separation 7.29 Å). In a similar way to **1**, the pyridyl groups are separated by a distance of 4.77 Å across the cyclobutane ring and lie splayed at an angle of approximately 82.7°. In contrast to **1**, however, the coordination geometry around each metal conforms to a square-pyramid, the coordination sites of the basal plane being occupied by two nitrogen atoms of two pyridines (N1 and N2), an oxygen atom of a sulfate ion (O1), and an oxygen atom of a water molecule (O5). The apical site is occupied by an oxygen atom of an additional sulfate ion (O2). In this arrangement, the sulfate ions serve to bridge two adjacent Cu centers,

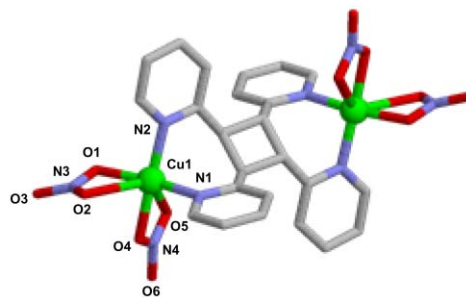


Fig. 1 Perspective of **1**. Selected interatomic distances (Å) and angles (°): Cu(1)–N(1) 1.970(7), Cu(1)–N(2) 1.993(7), Cu(1)–O(1) 1.969(6), Cu(1)–O(2) 2.637(7), Cu(1)–O(4) 2.022(6), Cu(1)–O(5) 2.394(6); N(1)–Cu(1)–N(2) 92.7(3), O(1)–Cu(1)–O(2) 54.0(3), O(4)–Cu(1)–O(5) 58.4(2) (colour scheme: grey = carbon; blue = nitrogen; red = oxygen; green = copper). Click image or here to access a 3D representation.

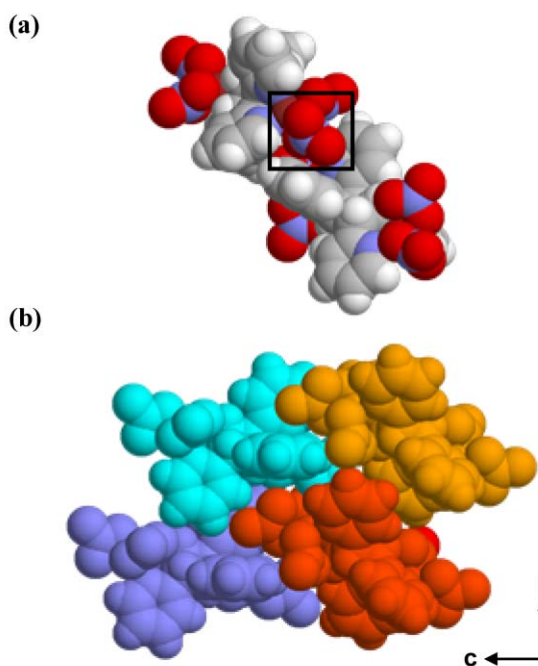


Fig. 2 View of the crystal structure of **1**: (a) 'tongue-and-groove' fit of the nitrate ion with the pyridyl units (colour scheme: white = hydrogen); and (b) 2D layered structure within the crystallographic *bc*-plane (adjacent complexes assigned individual colours for clarity).

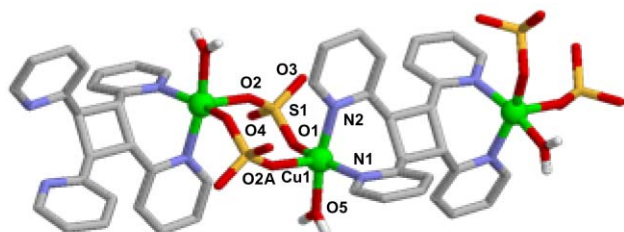


Fig. 3 Perspective of **2**. Selected interatomic distances (Å) and angles (°): Cu(1)–N(1) 2.017(2), Cu(1)–N(2) 2.002(2), Cu(1)–O(1) 1.971(2), Cu(1)–O(2)a 2.192(2), Cu(1)–O(5) 1.962(2); N(1)–Cu(1)–N(2) 87.4(1), O(1)–Cu(1)–O(2)a 104.2(1), N(1)–Cu(1)–O(5) 87.7(1), N(2)–Cu(1)–O(5) 168.0(1) (a: $-x + 1/2$, $-y + 1/2$, $-z$) (colour scheme: orange = sulfur). Click image or here to access a 3D representation.

forming, in a similar way to [Cu₄(3-(2-pyridyl)-triazino[5,6-*f*]1,10-phenanthroline)₂(SO₄)₂(H₂O)₁₀](SO₄)₂·4H₂O **3**,¹⁵ a chair-like, eight-membered ring. Notably, the Cu···Cu separation across the two sulfate ions of **2** (4.58 Å) is significantly shorter than that of **3** (4.90 Å). The ability of the cyclobutane unit and sulfate ion to bridge adjacent Cu atoms gives rise to, in a similar way to **3**, a 1D coordination polymer that runs along the *ac*-diagonal. Notably, in the case of **1**, both the charge and chelating behaviour displayed by the nitrate ion largely prohibit the formation of a similar extended structure.

A view of the crystal structure of **2**, as well as selected interatomic distances, is given in Fig. 4. The coordination polymer has crystallised with nine equivalents of water. Six water molecules (O6 thru O8) participate in an ordered array of O–H···O hydrogen bonds with either the coordinated water molecule or a sulfate ion [Fig. 4(a)]. The three remaining water molecules (O9 thru O10), which are related by symmetry, lie disordered adjacent to the pyridyl ligand, assembling by way of O–H···O forces with the ligated water. In a similar way to **1**, the splayed pyridyl groups of each chelating unit accommodate, in the case of **2**, a single pyridyl unit of an adjacent polymer strand by way of offset face-to-face π – π interactions (centroid···centroid distance 3.94 Å).¹⁶ As a consequence of these forces, adjacent polymer strands are oriented parallel and offset within

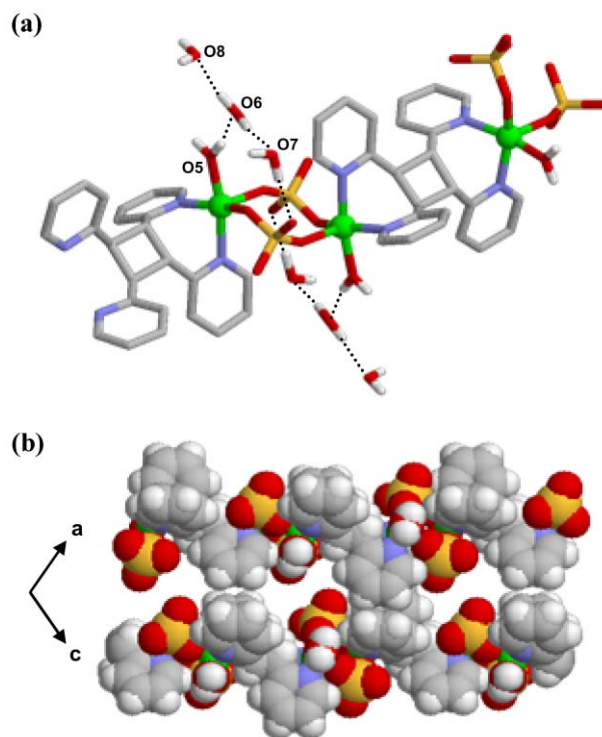


Fig. 4 View of the crystal structure of **2**: (a) the ordered water molecules involved in O–H···O hydrogen bonds with the 1D polymer; and (b) the packing of the polymer strands along the crystallographic *b*-axis (included water molecules omitted for clarity). Interatomic distances (Å) involving the ordered and disordered water molecules that participate in the hydrogen bonds: O(5)···O(6) 2.641(4), O(5)···O(9A) 2.554(4), O(5)···O(9B) 2.80(1), O(6)···O(8)a 2.810(3), O(6)···O(7) 2.792(4), O(7)···O(4) 2.841(4), O(7)···O(3)b 2.880(3), O(7)···O(9B)b 2.89(1), O(8)···O(4) 2.824(3), O(9A)···O(9B) 1.67(1), O(10)···O(9B) 1.82(1), O(9)···O(9)c 1.24(1) (a: x , $+y - 1$, z ; b: $-x + 1/2$, $y - 1/2$, $-z + 1/2$; c: $-x + 1$, y , $-z + 1/2$). Click image (b) or here to access a 3D representation.

2, producing 1D guest-filled channels that run parallel to the crystallographic *b*-axis [Fig. 4(b)]. The included guests, as well as the coordinated water molecules, are liberated from **2** by heating the solid to approximately 100 °C.

Conclusions

In this report, we have demonstrated an application of a product derived from a template-directed,^{5,6} solid-state,⁷ organic synthesis. In the present case, the product derived from the solid-state – 2,2'-tpcb – functions as a tetrafunctional bis-chelating ligand owing to the positioning of each nitrogen atom within each pyridyl ring and the separation of the pyridyl groups along the periphery of the cyclobutane unit. Efforts are currently underway to utilise additional products derived from the solid state for the construction of metal-based assemblies wherein such molecules may be used for the design of coordination arrays that display targeted properties (*e.g.* inclusion). An initial result has provided access to a porous metal–organic solid¹⁷ with channels stable to guest removal.¹⁸ In each case, the resulting complexes may be less available, or completely inaccessible in solution, providing access to latent¹⁹ coordination materials.

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