

# A lanthanide-based helicate coordination polymer derived from a rigid monodentate organic bridge synthesized in the solid state†‡

Dejan-Krešimir Bučar,<sup>a</sup> Giannis S. Papaefstathiou,<sup>b</sup> Tamara D. Hamilton<sup>a</sup> and Leonard R. MacGillivray<sup>\*a</sup>

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**Tetratopic *rectt*-tetrakis(4-pyridyl)cyclobutane acts as an angular bifunctional ligand that yields a single-stranded helicate coordination polymer based on a Ln(III) ion.**

The design and construction of helicates<sup>1</sup> (*i.e.* metal-containing helices) is of great interest in metallosupramolecular chemistry owing to their potential applications in areas such as optics,<sup>2–6</sup> catalysis,<sup>7,8</sup> and medicine.<sup>9–11</sup> Helicity in such a metallosupramolecular architecture is a result of the geometric and stereoelectronic preferences of the organic ligand and metal center.<sup>12,13</sup> Whereas the synthesis of helicates has been typically achieved using angular ditopic bridging ligands based on either flexible monodentate or rigid chelating units (*e.g.* quarterpyridine),<sup>14</sup> helicates based on angular rigid monodentate bridges (*e.g.* 1,3-benzenetricarboxylic acid) have been rare.<sup>15</sup> The fact that such constructions have been rare can be ascribed to subtle structure effects of the self-assembly process. Generally, the curvature of a helix is achieved by organic and metal components that, collectively, produce an angle between 0 and 180°. Whereas a flexible bridge can, *de facto*, afford a relatively wide range of angles to support a helix, rigid bridges are more restrictive (Scheme 1). This means that a self-assembly designed to afford a helix based on a rigid organic bridge will most likely succeed using a metal with a flexible coordination sphere. Chelating groups have been useful in this regard since the multiple binding sites of a chelator saturate the coordination sphere of a metal, and thus prohibit ancillary components (*e.g.* anions or solvent) from disrupting the assembly process.

In recent years, we have described a method to control [2+2] photodimerizations in organic solids using hydrogen bond-mediated self-assembly involving small molecules as linear templates.<sup>16</sup> Resorcinol and derivatives have been used to stack *trans*-1,2-bis(4-pyridyl)ethylene to react and form *rectt*-tetrakis(4-pyridyl)cyclobutane (4,4'-tpcb). We have shown that the tetrapyridine invariably acts as a 4-connected node

in a series of 2D metal–organic frameworks (MOFs), with topologies that conform to grids and are based on *d*-block transition metal ions [*e.g.* Cu(II)]. Each pyridyl group of each solid was coordinated to a metal.<sup>17,18</sup> Metal–organic polygons and polyhedra have also been obtained using other tetrapyridines obtained using our solid-state strategy. Similar to the MOFs, each pyridine was coordinated to a metal.<sup>19</sup>

Herein, we wish to report the synthesis and structural characterization of a single-stranded helicate coordination polymer based on 4,4'-tpcb. We show that only two of the four 4-pyridyl units of 4,4'-tpcb coordinate to metals of the helicate, which, in turn, enables the tetrapyridine to function as a rare rigid monodentate bridge of a helix (Scheme 2). The helicate is based on a Ln(III) cation in {[Pr(4,4'-tpcb)(Cl)<sub>3</sub>(CH<sub>3</sub>OH)(H<sub>2</sub>O)]·2(CH<sub>3</sub>OH)·(H<sub>2</sub>O)}<sub>∞</sub> (**1**). Our use of Ln(III) ions stem from the fact that such metals can afford coordination materials, with applications as luminescent materials, radiopharmaceuticals and MRI contrast agents. We also show that the self-assembly process based on 4,4'-tpcb and Pr(III) is sensitive to the nature of the counterion, with a 3D hydrogen-bonded network being realized in {[Pr(NO<sub>3</sub>)<sub>3</sub>(MeOH)<sub>1.58</sub>(H<sub>2</sub>O)<sub>2.42</sub>]·2(4,4'-tpcb)·0.84H<sub>2</sub>O}<sub>∞</sub> (**2**).

Compound **1** was prepared by the addition of a methanol solution of 4,4'-tpcb (36.4 mg, 0.1 mmol) to a methanol solution of PrCl<sub>3</sub>·6H<sub>2</sub>O (35.9 mg, 0.1 mmol; 8 ml methanol). The green solution was left to evaporate at room temperature. Green prismatic crystals of **1** suitable for single-crystal X-ray diffraction were obtained after 12 d (yield: 55%).§

A view of the crystal structure of **1** is shown in Fig. 1. The Pr(III) cation is heptacoordinated, with a coordination geometry that conforms to a pentagonal bipyramid. Two chlorine atoms occupy the apical sites of the bipyramid (Pr–Cl(1) 2.717(1), Pr–Cl(2) 2.723(1) Å), while the remaining chlorine atom (Pr–Cl(3) 2.743(1) Å), along with two 4-pyridyl groups (Pr–N(1) 2.661(3), Pr–N(2) 2.671(3) Å), occupy the base of the bipyramid. The latter chlorine atom lies between the 4-pyridyl groups. In this arrangement, the two pyridyl groups, which are from two different cyclobutane molecules, bridge two metal

<sup>a</sup> University of Iowa, Department of Chemistry, Iowa City, IA, USA. E-mail: len-macgillivray@uiowa.edu; Fax: +1 319-335-1270; Tel: +1 319-335-3504

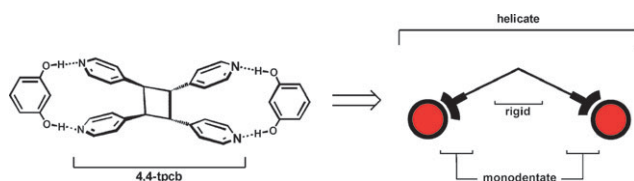
<sup>b</sup> Laboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepostimiopolis, Zografou 15771, Greece

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**Scheme 1** General roles of flexible monodentate and rigid chelating ligands in helicates.



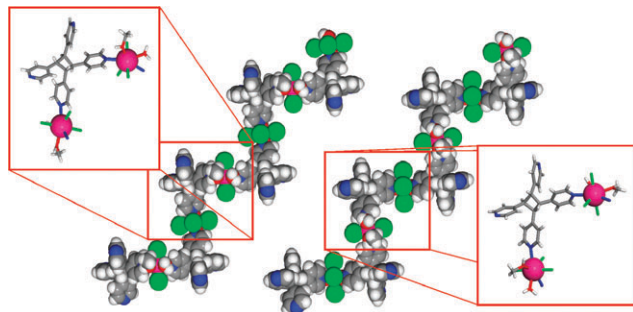
**Scheme 2** Templated synthesis of 4,4'-tpcb, and 4,4'-tpcb as a rigid ditopic monodentate ligand in a helicate.

centers. The bridging arises from two pyridyl groups that are *transoid* to each other. As a result, the cyclobutane acts as a bis-monodentate angular bridge, exhibiting a N–cyclobutane–N angle of 102.9°. As a consequence of these arrangements, the self-assembly of the ligands and the metal ions produces a single-stranded helical coordination polymer along a  $2_1$  screw axis. The pitch of the helix is 20.1 Å, and it contains two Pr(III) ions per turn, which are separated by 11.8 Å. Helices of both hands are present in the solid, being related by a center of inversion. **1** is a rare example of a helicate coordination polymer based upon a rigid organic bridge with monodentate units.

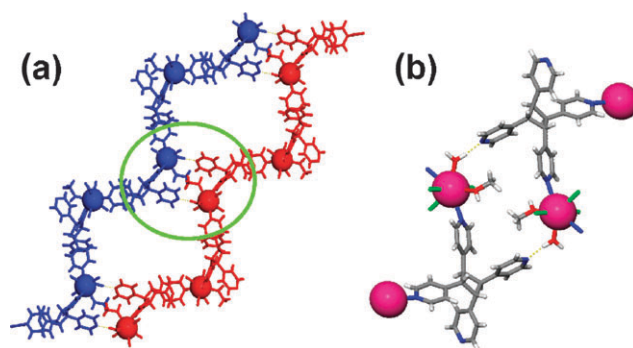
The fact that the tetrapyridine acts as a ditopic ligand means that two of the four pyridyl groups are not coordinated. These pyridyl groups participate in O–H...Ni (O(1)...N(3) 2.708(4) Å; i:  $-x + 1, -y + 2, -z + 1$ ) hydrogen bonds with the coordinated water molecules to form hydrogen-bonded dinuclear rhomboids. The rhomboids link helices of opposite handedness (*i.e.* left and right handed) in the solid (Fig. 2). The cavity of each rhomboid accommodates two coordinated methanol molecules. The edges of the rhomboids are defined by the pyridyl groups, while the corners are defined by two cyclobutane rings and two [Pr(MeOH)]<sup>3+</sup> units located at opposite corners (approximate corner distances: cyclobutane...cyclobutane 15.0 Å, Pr(III)...Pr(III) 8.8 Å). The solid also exhibits small voids occupied by highly disordered H<sub>2</sub>O and methanol molecules.

Compound **2** was obtained by dissolving PrNO<sub>3</sub>·6H<sub>2</sub>O (4.35 mg, 0.1 mmol) and 4,4'-tpcb (3.64 mg, 0.1 mmol) in methanol (8 ml), which produced a light green solution. Large green block crystals suitable for X-ray diffraction formed within 14 d upon solvent evaporation (yield: 68%).§

The structure of **2** reveals that the self-assembly of the helicate of **1** depends on the nature of the anion. In particular, the components of **2** have assembled to produce a 3D hydrogen-bonded network. As shown in Fig. 3, each metal is coordinated by three bidentate chelating NO<sub>3</sub><sup>−</sup> ions



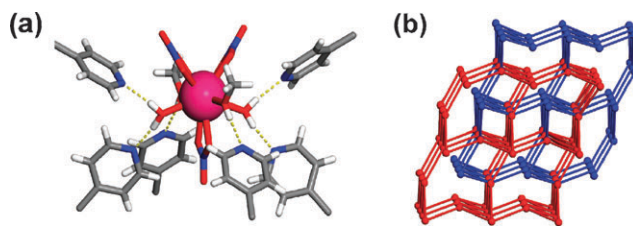
**Fig. 1** Space-filling models of left- and right-handed helicates of **1**.



**Fig. 2** Perspective view of: (a) left- and right-handed helicates (blue and red) that form a (b) hydrogen-bonded polygon.

(Pr–O(1) 2.597(2), Pr–O(2) 2.593(2), Pr–O(4), 2.662(2) Å), as well as two water molecules (Pr–O(6) 2.453(2) Å) (Fig. 2b). The remaining two sites are partially occupied by disordered methanol (Pr–O(7) 2.529(2); occupancy 79%) and water (Pr–O(8) 2.529(2); occupancy 21%) molecules. The metal ion is effectively decacoordinated. Indeed, it is likely that the chelating behavior of the NO<sub>3</sub><sup>−</sup> ions, as opposed to the chloride ion of **1**, precludes two molecules of 4,4'-tpcb from coordinating to the Pr(III) cation to support the formation of a helix. The structure of the 3D network is based on molecules of 4,4'-tpcb, which act as a 3-connected node, and complexes of [Pr(NO<sub>3</sub>)<sub>3</sub>(MeOH)<sub>1.58</sub>(H<sub>2</sub>O)<sub>2.42</sub>], which act as a 6-connected node, that interact *via* O–H...N<sub>pyridyl</sub> hydrogen bonds (O7(8)...N6 2.819(4), O6...N5<sup>i</sup> 2.759(4), O6...N3<sup>ii</sup> 2.750(3) Å; i:  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ; ii:  $x, y, z + 1$ ). As a result of these arrangements, the 3D hydrogen-bonded structure constitutes a two-fold interpenetrated binodal net, with a (4.6<sup>2</sup>)<sub>2</sub>(4<sup>2</sup>.6<sup>10</sup>.8<sup>3</sup>) topology (Fig. 3b).<sup>20,21</sup> To our knowledge, **2** is the first example of a self-assembled framework that conforms to this topology.<sup>21–23</sup> Channels are present in the solid, occupied by disordered water molecules, that run along both the crystallographic *c*-axis and [0 0 1]-plane. Collectively, the structure of **2** attests to the sensitivity of the self-assembly process; specifically, how the nature of the counterion can influence helix formation.

In conclusion, we have presented a helical coordination polymer based on a tetrapyridine molecule that acts as an angular and rigid monodentate bridging ligand. We have also shown that the self-assembly process is sensitive to the nature of the anion. The coordination polymer was achieved *via* a template-controlled solid-state organic synthesis, and using a metal center based upon a Ln(III) ion. Efforts are under way to



**Fig. 3** Perspective view of (a) the coordination and hydrogen bonds around the metal of **2**, and (b) the two-fold interpenetration of the 3D network.

further determine the factors that influence the self-assembly of the ligands obtained from the solid state into metal–organic frameworks and discrete structures.

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§ Crystal data for **1**:  $C_{27}H_{36}Cl_3N_4O_5Pr$ , orthorhombic, space group  $Pbcn$ ,  $a = 23.061(2)$ ,  $b = 13.596(1)$ ,  $c = 20.094(2)$  Å,  $V = 6300.3(1)$  Å<sup>3</sup>,  $D_c = 1.57$  g cm<sup>-3</sup>,  $Z = 8$ ,  $F(000) = 3008$ ,  $\mu = 1.84$  mm<sup>-1</sup>, Mo-K $\alpha$  radiation ( $\lambda = 0.71070$  Å),  $T = 190(1)$  K, 31701 collected reflections, 5528 unique reflections ( $R_{int} = 0.046$ ), 3227 observed reflections [ $I > 2\sigma(I)$ ],  $\theta_{max} = 25.0^\circ$ ,  $R_1(obs) = 0.025$ ,  $wR_2(obs) = 0.049$ ,  $R_2(all) = 0.044$ ,  $wR_2(all) = 0.046$ . The Fourier difference map revealed peaks that were identified as highly disordered water and methanol molecules. Despite the extensive use of restraints, attempts to resolve the disorder were unsuccessful, since the resulting model included unreasonably short intermolecular contacts. The electron contribution of the solvent molecules was therefore subtracted from the diffraction data using the SQUEEZE<sup>24</sup> procedure. The solvent molecules were determined to occupy 870.9 Å<sup>3</sup> or 13.8% of the unit cell. The total electron count of 211 electrons per unit cell corresponds to approximately one water and one methanol molecule. CCDC 674103.

Crystal data for **2**:  $C_{49.59}H_{52.85}N_{11}O_{13.84}Pr$ , monoclinic, space group  $C2/c$ ,  $a = 23.020(3)$ ,  $b = 16.869(2)$ ,  $c = 13.834(2)$  Å,  $\beta = 96.593(2)$ ,  $V = 5336.6(1)$  Å<sup>3</sup>,  $D_c = 1.45$  g cm<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 2388$ ,  $\mu = 0.987$  mm<sup>-1</sup>, Mo-K $\alpha$  radiation ( $\lambda = 0.71070$  Å),  $T = 200(1)$  K, 17468 collected reflections, 4637 unique reflections ( $R_{int} = 0.052$ ), 4081 observed reflections [ $I > 2\sigma(I)$ ],  $\theta_{max} = 25.0^\circ$ ,  $R_1(obs) = 0.033$ ,  $wR_2(obs) = 0.043$ ,  $R_2(all) = 0.070$ ,  $wR_2(all) = 0.072$ . CCDC 674104. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b800878g

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