

# An unprecedented 3D coordination network composed of two intersecting helices

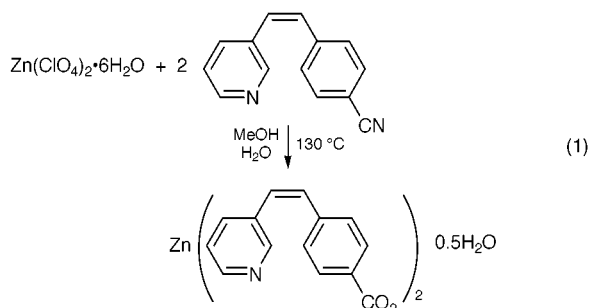
Owen R. Evans, Zhiyong Wang and Wenbin Lin\*

Department of Chemistry, Brandeis University, Waltham, MA 02454, USA. E-mail: wlin@brandeis.edu

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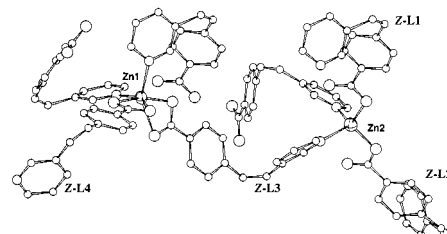
A hydro(solvo)thermal reaction between  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and *Z*-3-(4-cyanostyryl)pyridine affords an unprecedented chiral 3D coordination polymer  $\text{Zn}\{\text{Z}[\text{4-2-(3-pyridyl)ethenyl]benzoate}\}_2 \cdot 0.5\text{H}_2\text{O}$  with two intersecting six-fold helices, which shows a modest SHG activity owing to the essentially non-conjugate nature of the bridging ligand.

Chiral coordination networks are of great interest because of their potential utility in second-order nonlinear optical (NLO) applications,<sup>1</sup> chiral separations, and asymmetric catalysis.<sup>2</sup> Among many chiral structural motifs,<sup>3</sup> helices are of particular interest owing to their structural similarity to nucleic acids.<sup>4</sup> The chirality of such complexes has also shown potential in asymmetric catalysis.<sup>2</sup> We recently demonstrated the construction of acentric and chiral square grids using bifunctional *trans*-pyridylethenylbenzoate linking ligands.<sup>1</sup> In contrast, we believe that steric interactions in *cis*-pyridylethenylbenzoate will cause the pyridyl and phenyl group to significantly deviate from coplanarity. Such 'skewing' of coordination sites in the *cis*-pyridylethenylbenzoate should favor the formation of a helical structure. Herein we wish to report the synthesis and characterization of an unprecedented chiral 3D network resulting from the crosslinking of two distinct helices,  $\text{Zn}\{\text{Z}[\text{4-2-(3-pyridyl)ethenyl]benzoate}\}_2 \cdot 0.5\text{H}_2\text{O}$ , **1**.



Compound **1** was obtained in 60.5% yield by treating  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and *Z*-3-(4-cyanostyryl)pyridine under hydro(solvo)thermal conditions [eqn. (1)].<sup>5,6†</sup> The IR spectrum of **1** shows two strong symmetric C=O stretches at 1361 and 1400  $\text{cm}^{-1}$ , suggesting both monodentate and bidentate coordination of the carboxylate groups.<sup>7</sup> The formulation of **1** is supported by elemental analysis and thermogravimetric analysis results.<sup>8</sup>

A single crystal X-ray diffraction study of **1**† reveals an infinite 3D coordination polymer consisting of two distinct crosslinked helices. Compound **1** crystallizes in the chiral space group  $P3_2$ . The basic building block of **1** contains two crystallographically nonequivalent Zn atoms, four *Z*-[4-2-(3-pyridyl)ethenyl]benzoate (*Z*-L) ligands, and one solvated water molecule (Fig. 1).<sup>9</sup> The four *Z*-L ligands adopt two drastically different conformations: the *Z*-L<sup>1</sup> and *Z*-L<sup>2</sup> ligands are similar with a dihedral angle of 47.2 and 4.75° between the phenyl and pyridyl rings, while the dihedral angles for the *Z*-L<sup>3</sup> and *Z*-L<sup>4</sup> ligands are 70.3 and 70.1°. The Zn1 center adopts a *cis*-octahedral configuration by coordinating to the carboxylate groups of *Z*-L<sup>3</sup> and *Z*-L<sup>4</sup> in a semichelating fashion and to the pyridyl nitrogen atoms of *Z*-L<sup>1</sup> and *Z*-L<sup>2</sup>. In contrast, the Zn2

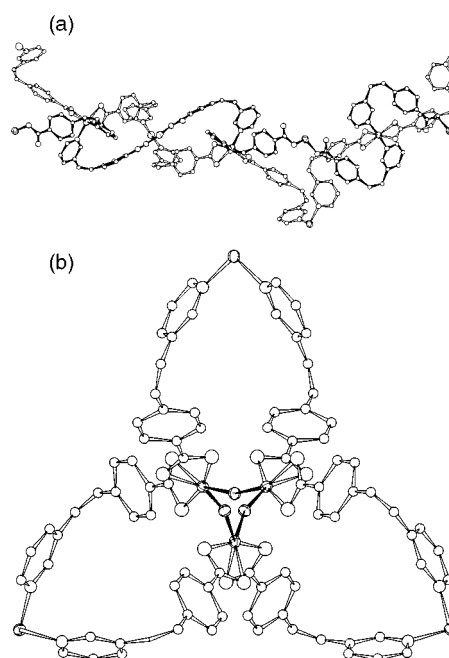


**Fig. 1** Coordination geometry in **1** of Zn1 and Zn2 centers. The ellipsoids represent zinc centers, while the circles with increasing sizes represent C, N and O, respectively. Zn1–O distances: 2.084(4), 2.086(5), 2.319(5), and 2.335(5) Å; Zn2–O distances: 1.954(4) and 1.956(4) Å. The Zn–N distances range from 2.03 to 2.08 Å.

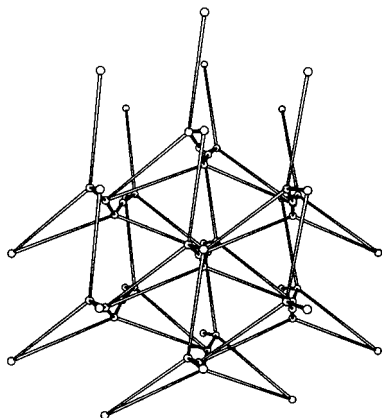
center adopts a tetrahedral geometry by coordinating to the carboxylate groups of *Z*-L<sup>1</sup> and *Z*-L<sup>2</sup> in a monodentate fashion and to the pyridyl nitrogen atoms of *Z*-L<sup>3</sup> and *Z*-L<sup>4</sup>.

The Zn1 and Zn2 centers are bridged by *Z*-L<sup>3</sup> and *Z*-L<sup>4</sup> to form an infinite sixfold helix parallel to the *c* axis (the Zn–Zn separations are 12.15 and 12.16 Å, respectively). The helices directed by the *Z*-L<sup>3</sup> and *Z*-L<sup>4</sup> are of the right-handed screw type and will be referred to as the primary helix (Fig. 2). The primary helix has a helical period of 44.18 Å, and each helical repeat contains three Zn1 and three Zn2 centers.

Conformationally similar *Z*-L<sup>1</sup> and *Z*-L<sup>2</sup> ligands serve to link Zn1 centers of a primary helix to Zn2 centers of adjacent primary helices. Each primary helix is covalently linked to six



**Fig. 2** A view of the cross-link between a primary helix and a secondary helix in **1** as shown down (a) the (111) face and (b) the *c* axis. The open bonds represent the primary helix, while the filled bonds represent the secondary helix. For clarity, the *Z*-L<sup>1</sup> and *Z*-L<sup>2</sup> ligands have been omitted in (b).



**Fig. 3** A perspective view of **1** slightly away from the *c* axis showing the 3D network resulting from the crosslinking of primary helices with secondary helices. Only Zn atoms are shown. The primary helices are represented as open bonds, while the secondary helices are represented as filled bonds.

neighboring primary helices. The Zn–Zn separations (7.47 and 7.49 Å) along the Z–L<sup>1</sup> and Z–L<sup>2</sup> bridges are significantly shorter than those along the Z–L<sup>3</sup> and Z–L<sup>4</sup> bridges. More interestingly, the connectivity propagated by Z–L<sup>1</sup> and Z–L<sup>2</sup> results in the formation of a secondary sixfold helix parallel to the *c* axis [Fig. 2(b)]. The secondary helix is of the left-handed screw type and crosslinks the primary helices to afford an infinite 3D network (Fig. 3).

Many discrete helical structures<sup>10</sup> and infinite helical coordination polymers<sup>11</sup> have been synthesized over the past decade. In some of these helical structures, neighboring helices are connected to each other *via* crosslinking to form 3D networks.<sup>12</sup> However, the structure of **1** is unprecedented in that the ‘crosslinks’ (the secondary helices) in **1** also display a helical-type structure. Both Zn1 and Zn2 centers in **1** are rendered chiral *via* coordination to the carboxylate and pyridyl functionalities of the bridging ligands. Linking of chiral repeats into a non-interpenetrated network has thus ensured the bulk chirality of **1**. Preliminary Kurtz powder second harmonic generation (SHG) measurements<sup>13</sup> indicated that **1** exhibits an expected modest powder SHG efficiency ( $I^{2\omega} = 6$  vs.  $\alpha$ -quartz) because of the non-conjugate nature of the Z–L ligand. Future work is directed toward the synthesis of efficient NLO materials *via* the incorporation of highly conjugated linking ligands.

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## Notes and references

† Preparation of Zn(C<sub>14</sub>H<sub>10</sub>NO<sub>2</sub>)<sub>2</sub>·0.5H<sub>2</sub>O: a heavy walled Pyrex tube containing a mixture of Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.045 g, 0.125 mmol) and Z-3-(4-cyanostyryl)pyridine (0.052 g, 0.5 mmol) in methanol (0.2 mL) and water (0.05 mL) was frozen and sealed under vacuum, and placed inside an oven at 120 °C. Colorless hexagonal crystals were obtained after 72 h of heating. Yield (0.040 g, 60.5%). Anal. calc. (found) for C<sub>28</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4.5</sub>Zn: C, 64.3 (64.1); H, 4.05 (4.04); N, 5.36 (5.59%).

‡ Crystal data for **1**: trigonal, space group *P*3<sub>2</sub>, *a* = 9.865(1), *c* = 44.179(2) Å, *U* = 3723.2(3) Å<sup>3</sup>, *Z* = 6, *D*<sub>c</sub> = 1.40 g cm<sup>-3</sup>, *T* = 173 K, Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å),  $\mu$  = 10.3 cm<sup>-1</sup>. Least-squares refinement based on 4589 reflections with *I* > 2 $\sigma$ (*I*) and 643 parameters led to convergence, with a final value of *R*1 = 0.045, *wR*2 = 0.098, and goodness of fit = 0.82. Flack parameter = -0.033(14). CCDC 182/1378.

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- Z-3-(4-cyanostyryl)pyridine was prepared in 27% yield by a room-temperature Wittig reaction between (4-cyanobenzyl)triphenylphosphonium bromide and 3-pyridinecarboxaldehyde with NaOH as the base in dichloromethane. The product was purified by silica gel column chromatography [hexane–ethyl acetate (1 : 1)].
- The slow hydrolysis of a cyanopyridine precursor to the desired pyridinecarboxylate ligand has been shown to be the key for the construction of polymeric coordination networks.<sup>1b</sup> Also see: O. R. Evans, Z. Wang, R.-G. Xiong, B. M. Foxman and W. Lin, *Inorg. Chem.*, 1999, **38**, 2969.
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- The solvated water molecule (O9) is *ca.* 3.5 Å away from both O1 and O3.
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