

A chiral interdigitated supramolecular network assembled from single-stranded helical tubes

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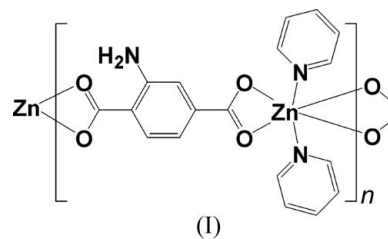
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The amino-functionalized helical chiral one-dimensional coordination polymer *catena*-poly[[bis(pyridine- κ N)zinc(II)]- μ -2-aminobenzene-1,4-dicarboxylato- $\kappa^4 O^1, O^1': O^4, O^4'$], $[Zn(C_8H_5NO_4)(C_5H_5N)_2]_n$, has an extended structure that is assembled from 2-aminobenzene-1,4-dicarboxylate anions and Zn^{2+} cations and which presents a left-handed 4_3 helix with a pitch of 25.6975 (9) Å. All the pyridine rings and all the amino groups point away from the helix to generate a hollow tube with a cross-section of approximately 8×8 Å running parallel to the crystallographic c direction. Each single-stranded helix is interdigitated with four neighbouring helices *via* N—H...O hydrogen bonds, which gives rise to a dense homochiral three-dimensional supramolecular network.

Comment

Considerable effort has been devoted to the synthesis and characterization of metal–organic coordination polymers because of their fascinating topologies and potential applications. One-dimensional coordination polymers, being the simplest topological type of coordination network, are commonly encountered in a number of forms, such as helices, ladders, ribbons and zigzag chains (Leong & Vittal, 2011). Extended helical coordination polymers have attracted growing interest because of their similarities to biological systems and because of their potential utility in enantioselective catalysis (Han & Hong, 2005; Zheng & Lu, 2010). Arguably the most important feature of a helix is its chirality, and to investigate this a number of helical chiral coordination polymers have been assembled using flexible chiral or achiral organic linkers (Anokhina & Jacobson, 2004; Cui *et al.*, 2003; Reger *et al.*, 2011; Yuan *et al.*, 2009). When achiral organic ligands are used, many successful examples of spontaneous

chiral induction have been reported in the literature (Balamurugan & Mukherjee, 2005; Ezuhara *et al.*, 1999; Han *et al.*, 2007; He *et al.*, 2007; Wang *et al.*, 2005).



For the lower-dimensional helical chiral coordination polymers, it is easy and desirable to incorporate functional properties at the metal centres or in the backbone of the organic linkers. Furthermore, it is possible to develop strategies for engineering higher-dimensional materials through supramolecular entanglement (Cui *et al.*, 2003; Han & Zhou, 2008; Leong & Vittal, 2011; Wang *et al.*, 2004). These entangled porous frameworks usually display tuneable flexibility, which is useful for various applications and is often associated

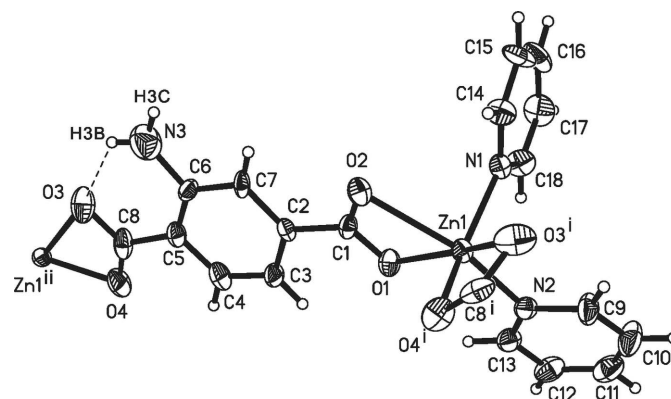


Figure 1

The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. [Symmetry codes: (i) $-y + 1, x + 1, z - \frac{1}{4}$; (ii) $y - 1, -x + 1, z + \frac{1}{4}$.]

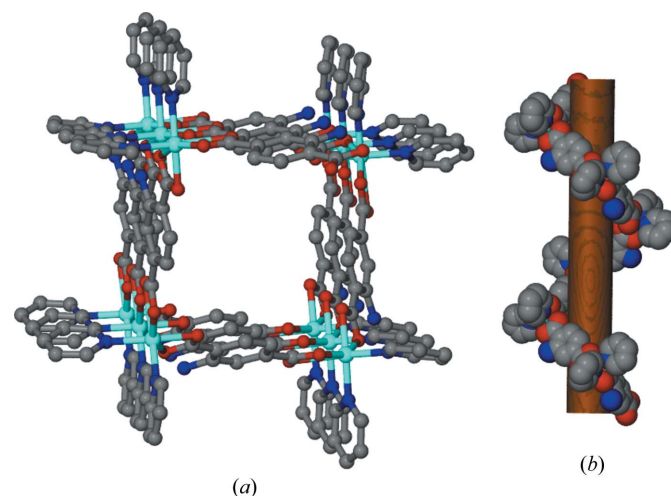


Figure 2

Views of (a) the one-dimensional helical tube and (b) left-handed helix of (I). All H atoms have been omitted for clarity.

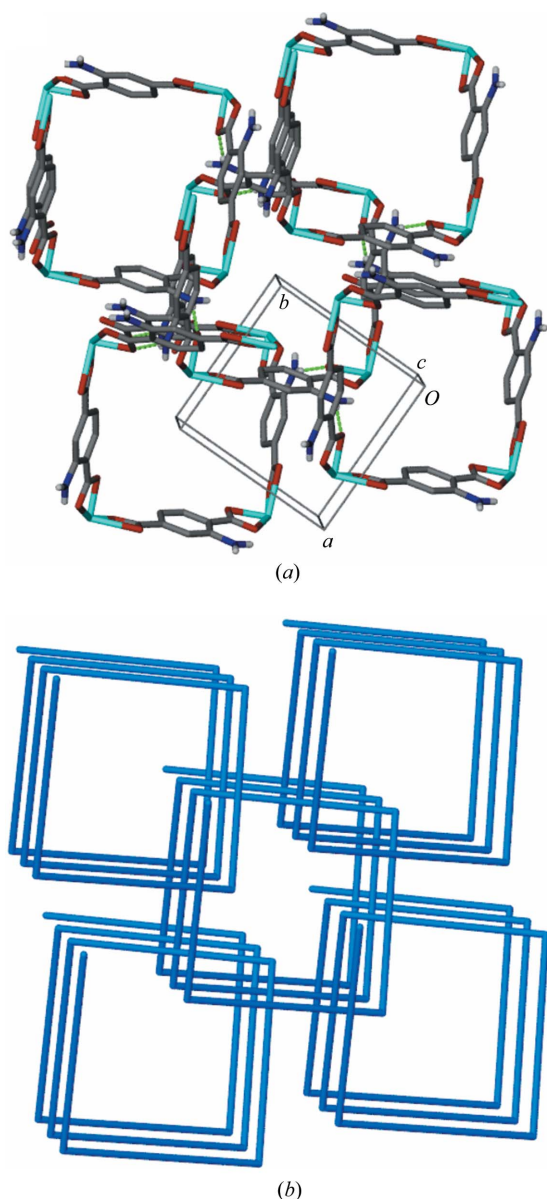


Figure 3
 (a) A view of the three-dimensional supramolecular network assembled from helices by N–H···O hydrogen bonds. All pyridine molecules and some of the H atoms have been omitted for clarity. (b) Schematic representation of the chiral interdigitated network of (I).

with weak interactions, including hydrogen bonds, π – π stacking and van der Waals interactions. In this study, we have synthesized a one-dimensional amino-functionalized helical chiral coordination polymer from achiral ligands; $[\text{Zn}(\text{NH}_2\text{-BDC})(\text{py})_2]_n$ ($\text{NH}_2\text{-BDC}$ is 2-aminobenzene-1,4-dicarboxylate and py is pyridine), (I), forms a three-dimensional interdigitated supramolecular network *via* N–H···O hydrogen bonds.

Colourless crystals of (I) were obtained following a hydrothermal synthesis using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2-aminobenzene-1,4-dicarboxylic acid and pyridine at 423 K for 3 d. Compound (I) crystallizes in the chiral space group $P4_3$ with one Zn^{2+} cation, one $\text{NH}_2\text{-BDC}$ anion and two pyridine ligands per asymmetric unit, as shown in Fig. 1. The Zn^{2+}

centre is coordinated by four O atoms from the carboxylate groups of two different $\text{NH}_2\text{-BDC}$ ligands and two mutually *cis* N atoms from the pyridine groups, giving a distorted octahedral geometry. The bond angles around the Zn^{2+} centre are given in Table 1. The Zn–O bond lengths range from 2.011 (3) to 2.480 (3) Å, a large spread, which is due to the highly asymmetric coordination mode adopted by the carboxylate groups. The amino group in the ligand backbone forms an N3–H3B···O3 intramolecular hydrogen bond (see Table 2). Amino-functionalized porous coordination frameworks have recently attracted much attention because of an enhanced capacity for CO_2 adsorption (Couck *et al.*, 2009; Vaidhyanathan *et al.*, 2009).

The coordination behaviour of the bridging $\text{NH}_2\text{-BDC}$ ligand of (I) results in an extended helical architecture running along the crystallographic *c* axis (Fig. 2). The left-handed helix is generated around the crystallographic 4_3 axis with a pitch of 25.6975 (9) Å. Each ‘turn’ of the helix consists of four Zn/ $\text{NH}_2\text{-BDC}$ units. All the pyridine rings and all the amino groups point away from the helical axis to generate a hollow tube with an opening of approximately 8×8 Å. Each left-handed helix interweaves with four similar helices and is linked to them *via* strong intermolecular N–H···O hydrogen bonds (see Table 2). These combine to give a dense three-dimensional interdigitated supramolecular network (Fig. 3). All helices have, of crystallographic necessity, the same left-handed chirality and run along the *c* direction. This leads to an enantiopure network, despite being formed solely from achiral molecular units. As no other crystals from the sample were analysed, it is not possible to determine whether the bulk sample is enantiomerically pure or a conglomerate containing both possible hands.

In conclusion, (I) is an interesting example of an amino-functionalized one-dimensional helical coordination polymer assembled from achiral ligands.

Experimental

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (92.6 mg, 0.5 mmol), 2-aminobenzene-1,4-dicarboxylic acid (149.6 mg, 0.5 mmol) and pyridine (1.0 g) in H_2O (5 ml) was sealed in a 25 ml Teflon-lined stainless steel reactor and heated at 423 K for 3 d. A crop of colourless single crystals of the title compound was obtained after cooling the solution to room temperature. Block-shaped crystals of (I) were collected and washed with distilled water. The yield was approximately 40% based on Zn^{2+} .

Crystal data

| | |
|--|---|
| $[\text{Zn}(\text{C}_8\text{H}_5\text{NO}_4)(\text{C}_5\text{H}_5\text{N})_2]$ | $Z = 4$ |
| $M_r = 402.70$ | Mo $K\alpha$ radiation |
| Tetragonal, $P4_3$ | $\mu = 1.37 \text{ mm}^{-1}$ |
| $a = 8.4243$ (1) Å | $T = 298 \text{ K}$ |
| $c = 25.6975$ (9) Å | $0.26 \times 0.24 \times 0.20 \text{ mm}$ |
| $V = 1823.72$ (7) Å ³ | |

Data collection

| | |
|---|--|
| Rigaku R-Axis RAPID diffractometer | 11175 measured reflections |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | 3172 independent reflections |
| $T_{\text{min}} = 0.716$, $T_{\text{max}} = 0.771$ | 2082 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.057$ |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|------------------------|-------------|--------------------------------------|-------------|
| Zn1—O1 | 2.011 (3) | Zn1—O4 ⁱ | 2.072 (5) |
| Zn1—N1 | 2.066 (4) | Zn1—O3 ⁱ | 2.296 (5) |
| Zn1—N2 | 2.069 (5) | Zn1—O2 | 2.480 (3) |
| O1—Zn1—N1 | 103.86 (15) | N2—Zn1—O3 ⁱ | 100.06 (17) |
| O1—Zn1—N2 | 98.92 (17) | O4 ⁱ —Zn1—O3 ⁱ | 59.46 (17) |
| N1—Zn1—N2 | 96.93 (19) | O1—Zn1—O2 | 56.93 (14) |
| O1—Zn1—O4 ⁱ | 101.20 (18) | N1—Zn1—O2 | 86.47 (15) |
| N1—Zn1—O4 ⁱ | 148.31 (19) | N2—Zn1—O2 | 155.54 (15) |
| N2—Zn1—O4 ⁱ | 98.03 (19) | O4 ⁱ —Zn1—O2 | 91.23 (15) |
| O1—Zn1—O3 ⁱ | 154.57 (18) | O3 ⁱ —Zn1—O2 | 104.13 (16) |
| N1—Zn1—O3 ⁱ | 90.48 (18) | | |

Symmetry code: (i) $-y + 1, x + 1, z - \frac{1}{2}$.**Table 2**

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| N3—H3B...O3 | 0.86 | 2.10 | 2.715 (8) | 128 |
| N3—H3C...O4 ⁱⁱ | 0.86 | 2.14 | 2.966 (9) | 162 |

Symmetry code: (ii) $-y, x + 1, z - \frac{1}{2}$.**Refinement** $R[F^2 > 2\sigma(F^2)] = 0.043$ $wR(F^2) = 0.071$ $S = 1.01$

3172 reflections

235 parameters

1 restraint

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.47 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.29 \text{ e } \text{Å}^{-3}$

Absolute structure: Flack (1983),

with 1546 Friedel pairs

Flack parameter: 0.030 (17)

All H atoms were positioned geometrically and allowed to ride on their respective parent atoms at distances of C—H = 0.93 Å and N—H = 0.86 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. Displacement ellipsoids indicate some considerable vibrational movement or disorder in the NH₂-BDC ligands, but we were unable to develop an alternative disorder model.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSO, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick,

2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KY3002). Services for accessing these data are described at the back of the journal.

References

- Anokhina, E. V. & Jacobson, A. J. (2004). *J. Am. Chem. Soc.* **126**, 3044–3045.
- Balamurugan, V. & Mukherjee, R. (2005). *CrystEngComm*, **7**, 337–341.
- Couck, S., Denayer, J. F. M., Baron, G. V., Rémy, T., Gascon, J. & Kapteijn, F. (2009). *J. Am. Chem. Soc.* **131**, 6326–6327.
- Cui, Y., Lee, S. J. & Lin, W. B. (2003). *J. Am. Chem. Soc.* **125**, 6014–6015.
- Ezuhara, T., Endo, K. & Aoyama, Y. (1999). *J. Am. Chem. Soc.* **121**, 3279–3283.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Han, L. & Hong, M. C. (2005). *Inorg. Chem. Commun.* **8**, 406–419.
- Han, L., Valle, H. & Bu, X. H. (2007). *Inorg. Chem.* **46**, 1511–1513.
- Han, L. & Zhou, Y. (2008). *Inorg. Chem. Commun.* **11**, 385–387.
- He, C., Zhao, Y. G., Guo, D., Lin, Z. H. & Duan, C. Y. (2007). *Eur. J. Inorg. Chem.* pp. 3451–3463.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Leong, W. L. & Vittal, J. J. (2011). *Chem. Rev.* **111**, 688–764.
- Reger, D. L., Horger, J. J., Smith, M. D., Long, G. J. & Grandjean, F. (2011). *Inorg. Chem.* **50**, 686–704.
- Rigaku (1998). *RAPID-AUTO*. Version 1.06. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSO (2004). *CrystalStructure*. Version 3.6.0. Rigaku/MSO, The Woodlands, Texas, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Vaidhyanathan, R., Iremonger, S. S., Dawson, K. W. & Shimizu, G. K. H. (2009). *Chem. Commun.* pp. 5230–5232.
- Wang, X.-L., Qin, C., Wang, E.-B., Xu, L., Su, Z.-M. & Hu, C.-W. (2004). *Angew. Chem. Int. Ed.* **43**, 5036–5039.
- Wang, Y.-T., Tong, M.-L., Fan, H.-H., Wang, H.-Z. & Chen, X.-M. (2005). *Dalton Trans.* pp. 424–426.
- Yuan, G. Z., Zhu, C. F., Liu, Y., Xuan, W. M. & Cui, Y. (2009). *J. Am. Chem. Soc.* **131**, 10452–10460.
- Zheng, X.-D. & Lu, T.-B. (2010). *CrystEngComm*, **12**, 324–336.