metal-organic papers

catena-Poly[[chloro(pyridinium-3-carboxylato-κO)zinc(II)]-μ-nicotinato-κ²O:N]

Mohamed Ghazzali,[a]*
Morsy A. M. Abu-Youssef[b] and
Vratislav Langer[a]

[a]Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden, and [b]Department of Chemistry, Faculty of Science, Alexandria University, PO Box 426, 21321 Alexandria, Egypt

Correspondence e-mail: mghazz@chalmers.se

The title bis-nicotinate zinc chloride, $[Zn(C_6H_4NO_2)Cl(C_6H_5NO_2)]_n$, has an infinite head-to-tail one-dimensional chain structure. The compound was synthesized under mild hydrothermal conditions. The Zn^{II} atom exhibits a distorted tetrahedral coordination geometry. The structure is statistically disordered, with 0.5 site occupancy for the Zn atom and the H atom located on the pyridine N atom. As a result, Zn positions in the crystal structure alternate between two sites related by a crystallographic twofold axis and rows of molecules are formed, supported by strong $N-H\cdots O$ hydrogen bonds.

Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.050
wR factor = 0.134
Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The architecture of solid-state materials, constructed from the directed self-assembly of metal centres with suitable organic spacers, has revealed different one-, two- and three-dimensional topologies with many fascinating properties (Desiraju, 1989; Öhrström & Larsson, 2005). Our ongoing interest is focused on the crystal engineering of hybrid structures constructed from transition metal ions with pyridinecarboxylate groups as the organic ligand (Abu-Youssef & Langer, 2006).

(I)
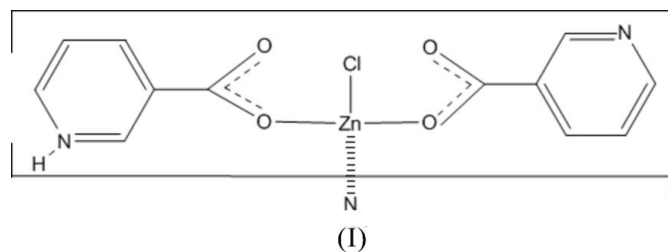
The structure of the title compound, (I), with the atomic numbering scheme is shown in Fig. 1. The structure shows statistical disorder, with 0.5 site occupancy for the Zn atom and the H atom located on N1. Selected bond distances and bond angles are given in Table 1.

The coordination around each Zn^{II} node can be described as highly distorted tetrahedral, with angles ranging from 90.79 (14) to 131.31 (9)°. As a result of the Zn-atom disorder, Zn positions in the crystal structure alternate between two sites related by the symmetry operation $(-x + 1, y, -z + \frac{1}{2})$. We present here a one-dimensional structure built up from head-to-tail patterns. The Zn^{II} centre is coordinated by two O atoms in two chelating carboxylate motifs from the two nicotinate spacers, with a dihedral angle between the mean planes of the carboxylate groups of 74.2 (4)°. The coordination is completed by a chloride ion and an N atom from the adjacent nicotinate ligand, arranged in a head-to-tail fashion, giving rise to rows of
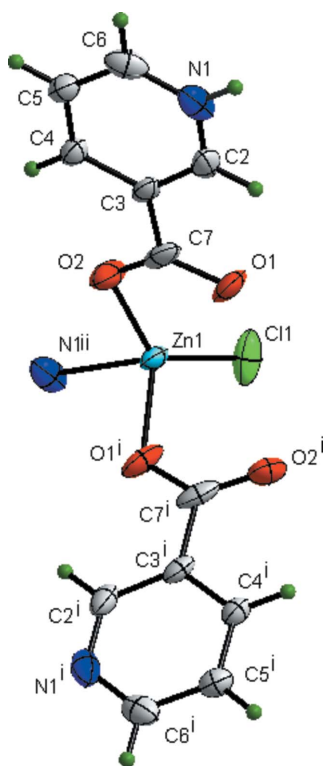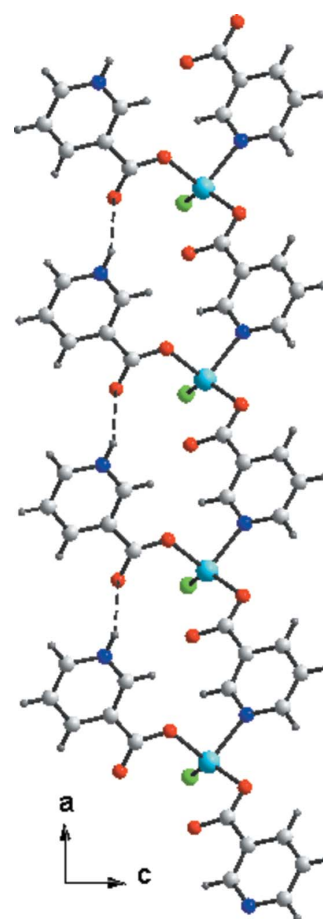
Figure 1
Part of the polymeric structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. For symmetry codes, see Table 1.

monomer units along the $[\frac{1}{2}, \frac{1}{2}, 0]$ vector, supported by strong N—H···O hydrogen bonds (Fig. 2 and Table 2). On the first-level graph set, as defined by Bernstein *et al.* (1995) and Grell *et al.* (1999), $C(6)$ chains are formed by these hydrogen bonds. Despite many dissimilarities between the present structure and that of [Zn(C₅H₄NCO₂H)(C₅H₄NCO₂)Cl] (Goher *et al.*, 1996) in the topology and the coordination environment of Zn^{II}, the Zn—Cl bond length is still retained, with a maximum difference of only 0.015 (3) Å.

Only four two- and three-dimensional topologies have been described for Zn^{II} with the nicotinate spacer (Lin *et al.*, 1998; Evans & Lin, 2001; Rather *et al.*, 2002; Wu *et al.*, 2004). To the best of our knowledge, this is the first example of a coordination mode between the Zn^{II} metal centre and nicotinate ligands, resulting in an infinite one-dimensional self-assembled network.

Experimental

To an aqueous solution (20 ml) of zinc chloride (0.27 g, 2 mmol, Aldrich), nicotinic acid (0.5 g, 4 mmol, Aldrich) in ethanol (15 ml) was added with continuous stirring. The solution became turbid and was then heated with stirring for 15 min, filtered twice and allowed to boil for 10 min. The resulting clear solution was allowed to stand at room temperature for 3–4 weeks. Transparent crystals of (I), suitable for X-ray diffraction, were collected by filtration and dried in air (yield 70%, m.p. 482–483 K). Spectroscopic analysis: IR (KBr pellet, ν, cm^{-1}): 3020 (C=C, *s*), 1742 (C=O, *s*), 1534 (C=C, *m*), 1395 (C—H, *s*), 1243 (C—N, *s*), 1062 (C—O, *m*), 764 (C—H, *m*).

Figure 2
A perspective drawing, showing rows of monomer units along the vector $[\frac{1}{2}, \frac{1}{2}, 0]$ with alternating positions of disordered Zn atoms. In this representation, Zn atoms are shown regularly spaced, but they are disordered as well as the hydrogen-bonded (dashed lines) pyridinium H atoms in the overall structure.

Crystal data

[Zn(C₆H₄NO₂)Cl(C₆H₅NO₂)]	$Z = 4$
$M_r = 346.03$	$D_x = 1.782$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 13.0493$ (2) Å	$\mu = 2.12$ mm^{-1}
$b = 7.7050$ (1) Å	$T = 173$ (2) K
$c = 12.9115$ (1) Å	Plate, colourless
$\beta = 96.439$ (1)°	$0.20 \times 0.08 \times 0.04$ mm
$V = 1290.00$ (3) Å^3	

Data collection

Siemens SMART CCD area-detector diffractometer	6430 measured reflections
ω scans	1341 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	1104 reflections with $I > 2\sigma(I)$
$T_{min} = 0.676$, $T_{max} = 0.920$	$R_{int} = 0.045$
	$\theta_{max} = 26.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.050$	$+ 5.3068P]$
$wR(F^2) = 0.134$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
1341 reflections	$\Delta\rho_{max} = 0.55$ e Å^{-3}
96 parameters	$\Delta\rho_{min} = -0.56$ e Å^{-3}
H-atom parameters constrained	

metal-organic papers

Table 1
Selected geometric parameters (Å, °).

Zn1—O2	1.924 (3)	Zn1—N1ii	2.104 (3)
Zn1—O1i	2.048 (3)	Zn1—Cl1	2.2061 (15)
O2—Zn1—O1i	108.91 (12)	O2—Zn1—Cl1	131.31 (9)
O2—Zn1—N1ii	90.79 (14)	O1i—Zn1—Cl1	115.15 (8)
O1i—Zn1—N1ii	93.14 (12)	N1ii—Zn1—Cl1	106.06 (1)

Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O2iii	0.88	2.15	2.870 (4)	139
C5—H5$\cdots$O1iv	0.95	2.44	3.302 (4)	151

Symmetry codes: (iii) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $x, -y + 1, z - \frac{1}{2}$.

H atoms were constrained to ideal geometry using an appropriate riding model, with C—H = 0.95 Å and with U_{iso}(H) = $1.2U_{eq}$(C).

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

References

Abu-Youssef, M. A. M. & Langer, V. (2006). *Polyhedron*, **25**, 1187–1194.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Brandenburg, K. (2005). *DIAMOND*. Version 3.1a. Crystal Impact GbR, Bonn, Germany.
Bruker (2003). *SMART* (Version 5.63), *SAINT* (Version 6.45) and *SHELXTL* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.
Desiraju, G. R. (1989). *Crystal Engineering: The Design of Organic Solids*, pp. 236–237. New York: Elsevier.
Evans, O. R. & Lin, W. (2001). *Chem. Mater.* **13**, 3009–3017.
Goher, M. A. S., Abu-Youssef, M. A. M. & Mautner, F. A. (1996). *Polyhedron*, **15**, 453–457.
Grell, J., Bernstein, J. & Tinhofer, G. (1999). *Acta Cryst.* B**55**, 1030–1043.
Lin, W., Evans, O. R., Xiong, R.-G. & Wang, Z. (1998). *J. Am. Chem. Soc.* **120**, 13272–13273.
Öhrström, L. & Larsson, K. (2005). *Molecule Based Materials: The Structural Network Approach*, pp. 19–34. Amsterdam: Elsevier.
Rather, B., Moulton, B., Walsh, R. D. B. & Zaworotko, M. J. (2002). *Chem. Commun.* pp. 694–695.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Wu, B., Yuan, D., Jiang, F., Wang, R., Han, L., Zhou, Y. & Hong, M. (2004). *Eur. J. Inorg. Chem.* pp. 2695–2700.