A one-dimensional zigzag coordination polymer: *catena*-poly[[diaquapyridinenickel(II)]-μ-pyridine-2,3-dicarboxylato-κ³N,O²:O³]

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The asymmetric unit of the title one-dimensional coordination polymer, $[Ni(C_7H_3NO_4)(C_5H_5N)(H_2O)_2]_n$, contains a quinolinate dianion, a nickel(II) ion, two water molecules and a pyridine molecule. The pyridine-2,3-dicarboxylate (quinolinate) ligands connect the nickel(II) ions in a head-to-tail fashion, resulting in the formation of a one-dimensional zigzag chain. Adjacent chains form pairs *via* an extensive network of hydrogen-bonding interactions. A weak C—H⋯O intermolecular hydrogen bond links neighboring pairs of chains, thus generating two-dimensional double-sheet layers that are stabilized *via* π–π-stacking interactions between adjacent quinolinate pyridyl rings.

Comment

The design and synthesis of new coordination polymers based on transition metal compounds and multidentate organic ligands have attracted much interest in recent years because of the intriguing molecular topologies of these polymers and their potential applications as novel functional materials (Batten & Robson, 1998; Hagrman *et al.*, 1999). One of the major goals in the field of polymeric chemistry is to gain control over the structure of the infinite array itself, as well as to be able to control the packing arrangement of the polymeric entities in the solid-state structure (Moulton & Zaworotko, 2001). In order to establish general principles for more complicated systems, it is useful first to exploit the simplest topological type of coordination polymers, *i.e.* one-dimensional chain-like structures (Khlobystov *et al.*, 2001). In general, it is possible to assemble an infinite structure from a linear multidentate ligand, such as 4,4′-bipyridine (Robinson & Zaworotko, 1995) or 1,4-benzenedicarboxylate (Li *et al.*,

1999), together with suitable metal ions. In some cases, non-linear multidentate ligands, such as quinolinate (pyridine-2,3-dicarboxylate), can also be good linkers, because they can tolerate a distortion in their molecular geometry that results in an expansion of the angle between their coordination sites (Gutschke *et al.*, 1995; Jaber *et al.*, 1996; Sileo *et al.*, 1999). We report here the structure of such a quinolinate-containing zigzag chain-like coordination polymer, namely *catena*-poly-[[diaquapyridinenickel(II)]-μ-pyridine-2,3-dicarboxylato-κ³N,O²:O³], (I).

(I)
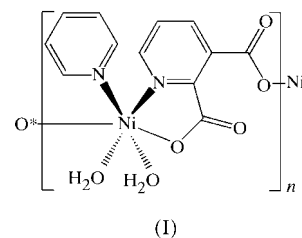
As shown in Fig. 1, the Ni^{II} atom adopts a slightly distorted octahedral geometry and is coordinated to four O atoms, of which two [atoms O1 and O4^i; symmetry code: (i) $x, y, 1 + z$] belong to the two carboxylate groups on the quinolinate ligand and two are from water molecules (Table 1). Two N atoms complete the sixfold coordination sphere around the metal ion, *viz.* pyridine atom N1 and pyridyl atom N2 of the quinolinate ligand. Thus, the quinolinate ligand acts as a bridge, *via* atom O4, linking neighboring Ni^{II} atoms in a head-to-tail fashion, resulting in an infinite zigzag chain running along the c axis. The O1/C11/O3 carboxylate group is coplanar with the pyridyl plane, but steric interaction between the two carboxylate groups forces the O2/C12/O4 group to lie almost perpendicular to the pyridyl ring, with a dihedral angle of 86.43 (8)° between the pyridyl and the carboxyl planes. The pyridine ligand coordinates to the Ni^{II} atom along an axial direction of the distorted octahedron, with atom O2W below the equatorial plane. Consecutive equatorial planes (Ni, O1, O2W, N2 and O4^i) in the chains are coplanar. The elongation
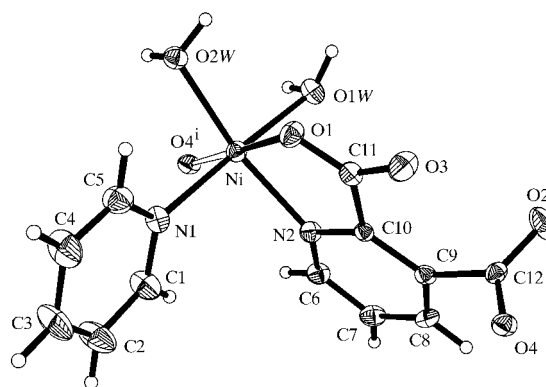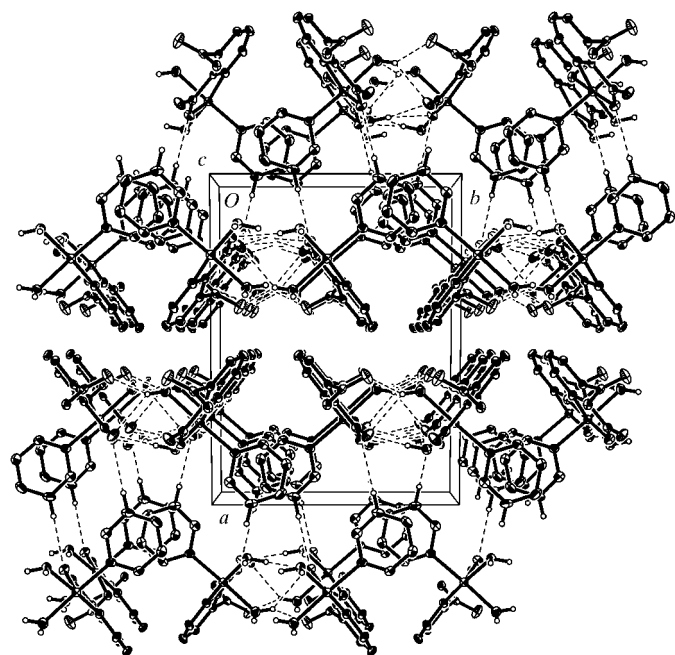
Figure 1
The asymmetric unit of (I) (solid lines), with displacement ellipsoids shown at the 30% probability level. [Symmetry code: (i) $x, y, 1 + z$.]
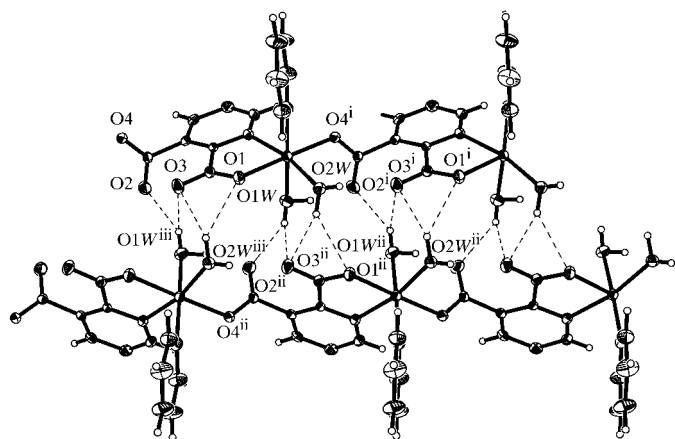
Figure 2
A perspective view of the hydrogen bonds generating a pair of chains. H atoms unrelated to these hydrogen bonds have been omitted for clarity. [Symmetry codes: (i) $x, y, 1 + z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x, \frac{1}{2} - y, -\frac{1}{2} + z$.]

of the bond distance between the two Csp^2 atoms (C10—C11) has also been observed for an earlier metal–quinolinate coordination polymer (Jaber *et al.*, 1996). Similar bond distances have been reported for related compounds in previous studies [1.538 (9) (Ravikumar *et al.*, 1995) and 1.535 (3) Å (Neels *et al.*, 1997)].

The packing structure of (I) is dominated by extensive hydrogen bonding (Table 2). There are two intrachain hydrogen bonds, namely O1W—H1WB···O2^{i} and O2W—H2WA···O3^{i}, which participate in controlling the conforma-

Figure 3
A packing diagram of (I), viewed along the *c* axis, illustrating the weak hydrogen bonds along *a* and interlayer π–π interactions. H atoms not involved in hydrogen bonding have been omitted for clarity.

tion of the chains extending along the *c* axis. Two adjacent chains are connected along the *b* axis, thus forming a pair of chains *via* four interchain hydrogen bonds [O1W—H1WA···O2^{ii}, O1W—H1WA···O3^{ii}, O2W—H2WB···O1^{ii} and O2W—H2WB···O3^{ii}; symmetry code: (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$], as depicted in Fig. 2. The Ni···Ni intrachain distance is 7.667 (2) Å, whereas the Ni···Ni interchain distance is shorter [6.265 (2) Å].

A weak C4—H4···O1($-x$, $1 - y$, $-z$) hydrogen bond connects the chains approximately along the *a* axis in an antiparallel mode, forming a two-dimensional double sheet in the *bc* plane, with the sheets layered along the *c* axis (Fig. 3). The centroid–centroid distance between two adjacent quinolinate pyridyl rings in different layers is 3.861 (1) Å, indicating the presence of π–π-stacking interactions between the two-dimensional double-sheet layers (Janiak, 2000). In contrast, the centroid–centroid distance between the pyridine rings of two adjacent pairs of molecules stacked along the *c* axis is 4.016 (8) Å, indicating that there is no π–π interaction.

Experimental

Ni(ClO$_4$)$_2$·6(H$_2$O) (109.6 mg, 0.30 mmol), quinolinic acid (51.3 mg, 0.30 mmol) and pyridine (0.4 ml) were dissolved in a mixture of water (6 ml) and ethanol (3 ml). The mixture was placed in a Teflon-lined stainless steel vessel (25 ml), which was sealed and heated to 403 K and then cooled to room temperature after 72 h. Blue block-like crystals were collected by filtration and were then washed with water and ethanol to afford (I) (yield ~80%).

Crystal data

[Ni(C$_7$H$_3$NO$_4$)(C$_5$H$_5$N)(H$_2$O)$_2$]	$D_x = 1.699$ Mg m^{-3}
$M_r = 338.95$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 15.240$ (3) Å	reflections
$b = 11.424$ (2) Å	$\theta = 1.3$–$13.5°$
$c = 7.6670$ (15) Å	$\mu = 1.49$ mm^{-1}
$\beta = 96.79$ (3)°	$T = 298.4$ (2) K
$V = 1325.5$ (5) Å^3	Block, blue
$Z = 4$	$0.13 \times 0.12 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4	1356 reflections with $I > 2\sigma(I)$
diffractometer	$R_{\text{int}} = 0.043$
ω scans	$\theta_{\text{max}} = 25.0°$
Absorption correction: ψ scan	$h = -18 \rightarrow 17$
(*XCAD*4; Harms & Wocadlo,	$k = -13 \rightarrow 0$
1995)	$l = 0 \rightarrow 9$
$T_{\text{min}} = 0.819$, $T_{\text{max}} = 0.860$	3 standard reflections
2520 measured reflections	every 200 reflections
2326 independent reflections	intensity decay: 1.0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.103$	$(\Delta/\sigma)_{\text{max}} = 0.050$
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.36$ e Å^{-3}
2326 reflections	$\Delta\rho_{\text{min}} = -0.37$ e Å^{-3}
206 parameters	
H atoms treated by a mixture of	
independent and constrained	
refinement	

Table 1
Selected geometric parameters (Å, °).

Ni—O1	2.023 (3)	C10—N2	1.362 (6)
Ni—O4^i	2.058 (3)	C10—C11	1.527 (7)
Ni—N1	2.089 (4)	C11—O1	1.242 (5)
Ni—N2	2.062 (4)	C11—O3	1.240 (6)
Ni—O1W	2.093 (4)	C12—O2	1.240 (6)
Ni—O2W	2.077 (4)	C12—O4	1.252 (6)
O1—Ni—N1	91.80 (16)	O1—Ni—O1W	88.31 (16)
O1—Ni—N2	80.40 (15)	O2W—Ni—N1	92.05 (17)
O1—Ni—O2W	88.67 (15)	O2W—Ni—O1W	90.36 (15)
O4^i—Ni—N2	99.79 (14)	O4^i—Ni—N1	89.76 (15)
O4^i—Ni—O2W	91.00 (14)	O4^i—Ni—O1W	90.14 (15)
N2—Ni—N1	93.16 (17)	N2—Ni—O1W	84.48 (16)
C8—C9—C12—O2	90.7 (6)	C10—C9—C12—O4	97.0 (6)

Symmetry code: (i) $x, y, 1 + z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1WB$\cdots$O2^i	0.89 (3)	1.71 (3)	2.586 (5)	167 (5)
O1W—H1WA$\cdots$O2^{ii}	0.88 (2)	2.20 (4)	2.885 (6)	134 (5)
O1W—H1WA$\cdots$O3^{ii}	0.88 (2)	2.37 (4)	3.073 (6)	138 (5)
O2W—H2WB$\cdots$O1^{ii}	0.88 (3)	2.44 (3)	3.173 (5)	141 (4)
O2W—H2WA$\cdots$O3^i	0.86 (3)	1.93 (2)	2.790 (5)	173 (5)
O2W—H2WB$\cdots$O3^{ii}	0.88 (3)	2.16 (3)	3.010 (5)	162 (4)
C4—H4$\cdots$O1^{iii}	0.93	2.55	3.473 (7)	172

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

H atoms bonded to C atoms were introduced at calculated positions and treated as riding, with C—H distances of 0.93 Å. All of the water H atoms were found in difference maps at an intermediate stage of the refinement and were refined subject to an O—H DFIX restraint (*SHELXL*97; Sheldrick, 1997) of 0.88 (3) Å and an angular H—O—H restraint [H—H = 1.39 (3) Å]. The U_{iso} values of the water H atoms were refined, but in all other cases, the U_{iso}(H) value was taken to be $1.2U_{eq}$ of the parent atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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