

A single-strand helical coordination polymer: *catena*-poly[[[triaqua-nickel(II)]- μ -2,2'-bipyridine-3,3'-dicarboxylato- κ^3 N,N':O] monohydrate]

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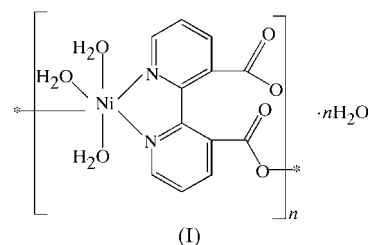
The asymmetric unit of the title compound, $\{[\text{Ni}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}\}_n$, is composed of a lattice water molecule and a nickel(II) ion that is coordinated by three water molecules and the two N atoms of a 2,2'-bipyridine-3,3'-dicarboxylate ligand. The twist of the 2,2'-bipyridine-3,3'-dicarboxylate unit and the coordination of one carboxylate group to a symmetry-related Ni^{II} atom generate a helical chain that runs along the *b* axis. Intrahelical hydrogen bonds participate in controlling the orientation of the helices, and both right-handed and left-handed helices are connected by interhelical hydrogen bonds into two-dimensional sheets.

Comment

Helical structures have attracted considerable attention in fields as diverse as biochemistry and materials science (Engelkamp *et al.*, 1999; Seo *et al.*, 2000, and references therein; Gangopadhyay & Radhakrishnan, 2001). In artificial supramolecular architectures, helicity can be introduced by conformational restrictions of inter- or intramolecular hydrogen bonds and coordination to metal ions (Piguet *et al.*, 1997), and for supramolecular coordination compounds, the formation of helices depends on the nature of the metal and ligands. It is also well known that a chiral structure can often lead to the formation of a helical structure (Albrecht, 2001). Some 2,2',6,6'-tetrasubstituted biphenyl compounds and 1,1'-binaphthalene derivatives can be twisted, and in a chiral structure, because of the steric effect of substituting groups, a helical structure can be formed when the molecules are connected in an appropriate way (Minuti *et al.*, 1999; Hamblin *et al.*, 2002). The same is true of some 2,2'-bipyridine derivatives when they are coordinated to metal ions (Kaes *et al.*, 2000; Tynan *et al.*, 2003). We report here the structure of a one-

dimensional helical coordination polymer, *viz.* the title compound, (I).

As shown in Fig. 1, the asymmetric unit of (I) consists of an Ni^{II} atom, a 2,2'-bipyridine-3,3'-dicarboxylate dianionic ligand, three coordinated water molecules and a non-coordinated water molecule. The coordination sphere of atom Ni1 can be described as a slightly distorted octahedron involving three water O atoms (O1W, O2W and O3W), a fourth O atom, O3($\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$), from a coordinated carboxylate group, and two N atoms (N1 and N2) from the 2,2'-bipyridine unit, which acts as a chelating ligand. The Ni1–O bond distances are in the range 2.037 (3)–2.092 (3) Å (Table 1). The 2,2'-bipyridine unit is twisted, with an N1–C5–C6–N2 torsion angle of 29.0 (4)°, such that the two carboxylate groups are located *trans* to each other. The C12/O3/O4 and C11/O1/O2 carboxylate groups are also twisted from their attached pyridyl planes, with dihedral angles of 37.4 (5) and 42.3 (3)°, respectively, for the N1/C1–C5 and N2/C6–C10 pyridyl rings. Similar distortions of the ligand molecule are observed in some transition metal complexes (Ravikumar *et al.*, 1995; Zhang *et al.*, 2002).



One of the two carboxylate groups is bound to the nickel(II) ion in a monodentate fashion in the axial direction of the distorted octahedron, while the base plane defined by atoms O1W, O3W, N1 and N2 is an equatorial plane. Furthermore, the twisted 2,2'-bipyridine–Ni chelating units (C1–C5/N1/Ni/N2/C6–C10) pack in an alternate reverse

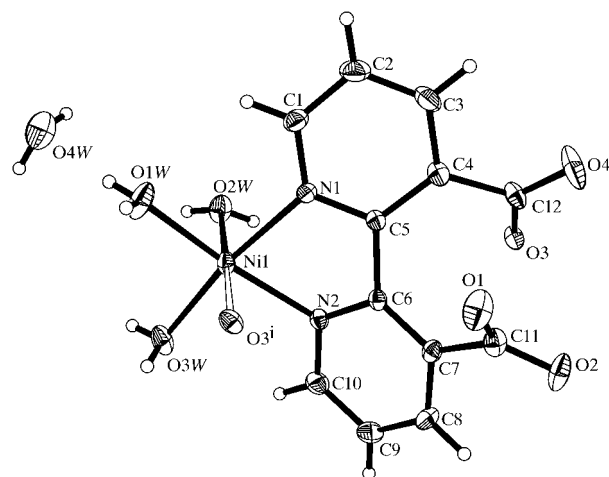


Figure 1

A view of the molecular structure of (I), showing the asymmetric unit (solid lines), with displacement ellipsoids at the 30% probability level. [Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.]

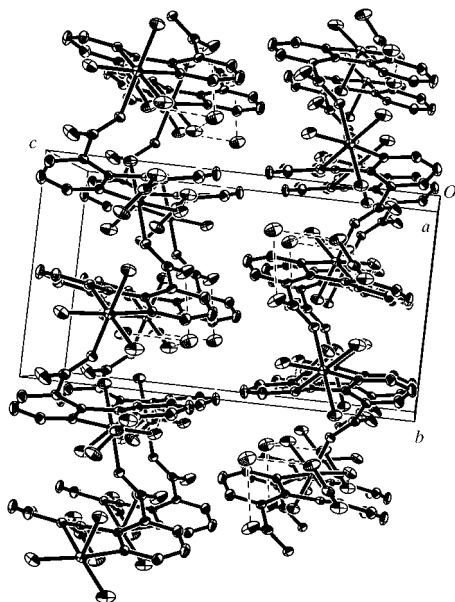


Figure 2
The crystal packing of the two types of two-dimensional sheet formed by the hydrogen-bond connections to the helices. H atoms have been omitted for clarity.

order and, therefore, the connections of the coordinated carboxyl O atoms generate a helix that propagates along the *b* axis. There are two types of helix, *viz.* right-handed and left-handed, which are related by an inversion center.

All uncoordinated carboxylate O atoms are linked to water molecules. Helices of the same type are connected by five hydrogen bonds, *viz.* O1W—H1WA···O4W, O4W—H4WA···O1ⁱⁱ, O4W—H4WB···O4ⁱⁱ, O3W—H3WA···O2ⁱⁱ and O2W—H2WA···O4ⁱⁱ [symmetry code: (ii) $x - 1, y, z$; Table 2]. Thus, the lattice water molecule serves as a bridge, together with another two direct interhelical hydrogen bonds, that joins adjacent helices of the same type, so forming a two-dimensional layer that runs along the *a* axis. Moreover, there are three intrahelical hydrogen bonds, *viz.* O3W—H3WB···O4ⁱ, O1W—H1WB···O2ⁱ and O2W—H2WB···O1ⁱⁱⁱ [symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; Table 2], which connect the main asymmetric units (without the lattice water molecule) and participate in controlling the orientation of the helix. In the lattice, the right-handed layers and the left-handed layers alternate along the *c* axis *via* the intermolecular interactions, as shown in Fig. 2.

Experimental

Ni(ClO₄)₂·6H₂O (83.9 mg, 0.23 mmol), 2,2'-bipyridine-3,3'-dicarboxylic acid (24.3 mg, 0.10 mmol) and pyridine (0.2 ml) were dissolved in a mixture of water (7 ml) and ethanol (2.5 ml). The solution was placed in a Teflon-lined stainless steel vessel (25 ml), which was sealed and heated at 413 K for 72 h under autogeneous pressure and then cooled to room temperature. Large blue rod-like crystals were collected by filtration and washed with water and ethanol (yield ~46%).

Crystal data

[Ni(C₁₂H₆N₂O₄)(H₂O)₃]₂·H₂O
M_r = 372.96
 Monoclinic, *P*2₁/*n*
a = 9.931 (2) Å
b = 9.1780 (18) Å
c = 15.970 (3) Å
 β = 96.71 (3)°
V = 1445.6 (5) Å³
Z = 4

D_x = 1.714 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 2.2–14.5°
 μ = 1.39 mm⁻¹
T = 298.4 (2) K
 Rod, blue
 0.32 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: ψ scan (XCAD4; Harms & Wocadlo, 1995)
T_{min} = 0.583, *T_{max}* = 0.870
 2672 measured reflections
 2518 independent reflections

1795 reflections with *I* > 2σ(*I*)
R_{int} = 0.047
 θ_{\max} = 25.0°
h = 0 → 11
k = 0 → 10
l = -18 → 18
 3 standard reflections every 200 reflections
 intensity decay: 1.0%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.037
wR (*F*²) = 0.090
S = 1.03
 2518 reflections
 240 parameters
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0201P)^2 + 2.1522P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.61 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1—O1W	2.037 (3)	O3—C12	1.244 (4)
Ni1—O3W	2.051 (3)	N1—C5	1.344 (4)
Ni1—O3 ⁱ	2.055 (3)	N2—C6	1.357 (4)
Ni1—N1	2.056 (3)	C4—C12	1.524 (5)
Ni1—N2	2.088 (3)	C5—C6	1.487 (5)
Ni1—O2W	2.092 (3)		
O1W—Ni1—O3W	95.58 (14)	N1—Ni1—N2	78.44 (11)
O1W—Ni1—O3 ⁱ	88.56 (13)	O1W—Ni1—O2W	90.33 (15)
O3W—Ni1—O3 ⁱ	90.69 (12)	O3W—Ni1—O2W	89.70 (14)
O1W—Ni1—N1	93.15 (13)	O3 ⁱ —Ni1—O2W	178.85 (12)
O3 ⁱ —Ni1—N1	87.96 (11)	N1—Ni1—O2W	91.82 (12)
O3W—Ni1—N2	92.71 (12)	N2—Ni1—O2W	96.46 (13)
O3 ⁱ —Ni1—N2	84.60 (11)		

Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

Table 2

Hydrogen-bonding 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>
O4W—H4WB···O4 ⁱⁱ	0.81 (7)	2.20 (8)	2.850 (5)	139 (7)
O4W—H4WA···O1 ⁱⁱ	0.89 (7)	1.97 (7)	2.846 (6)	171 (6)
O3W—H3WB···O4 ⁱ	0.84 (6)	1.91 (6)	2.704 (5)	159 (6)
O3W—H3WA···O2 ⁱⁱ	0.78 (5)	1.89 (5)	2.641 (4)	162 (5)
O2W—H2WA···O4 ⁱⁱ	0.85 (5)	2.58 (5)	3.263 (5)	138 (4)
O2W—H2WB···O1 ⁱⁱⁱ	0.83 (5)	1.90 (5)	2.716 (5)	169 (5)
O1W—H1WA···O4W	0.80 (4)	1.87 (5)	2.668 (5)	175 (5)
O1W—H1WB···O2 ⁱ	0.85 (6)	1.86 (6)	2.707 (5)	176 (5)

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $x - 1, y, z$; (iii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$.

H atoms bonded to C atoms were introduced at calculated positions and treated as riding, with *U_{iso}*(H) values equal to 1.2*U_{eq}*(C) and C—H distances of 0.93 Å. All water H atoms were located from difference maps at the final stages of the refinement and were refined freely.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1420). Services for accessing these data are described at the back of the journal.

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