

Pentaaqua(μ -pyridine-2,6-dicarboxylato-*N,O,O',O''*)(pyridine-2,6-dicarboxylato-*N,O,O''*)dinickel(II) dihydrate

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$

R factor = 0.041

wR factor = 0.112

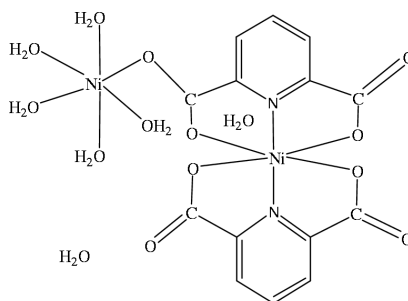
Data-to-parameter ratio = 10.6

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

The title compound, $[\text{Ni}_2(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_5]\cdot 2\text{H}_2\text{O}$, was obtained by the reaction of nickel iodide with dipicolinic acid (pyridine-2,6-dicarboxylic acid) and 1,10-phenanthroline (molar ratio 1:1:1) in EtOH/H₂O. The compound contains two six-coordinated Ni^{II} ions, which are linked by two O atoms of the same carboxyl group from dipicolinic acid [$\text{Ni}-\text{O}$ 2.179 (3) and 2.038 (3) Å]. Molecules are connected by van der Waals interactions.

Comment

The complexation of metal ions by dipicolinic acid (pyridine-2,6-dicarboxylic acid) has been extensively studied (Cousson *et al.*, 1992; Laine *et al.*, 1995*a,b*). Owing to the unique ability of the ligand to form stable chelates with various coordination modes and its biological activity, many crystal structures have been determined. In these complexes, dipicolinic acid acts as a tridentate ligand by coordination of the N atom and one O atom from each carboxylate group. Dipicolinic acid is thus a multi-chelating ligand capable of forming monomeric or polymeric complexes (Guerriero *et al.*, 1987; Kjell *et al.*, 1993; Abboud *et al.*, 1998). We report here the synthesis and crystal structure of a dinuclear nickel dipicolinate compound, (I).



(I)

In the title compound, (I), the atom Ni1 is octahedrally coordinated by two tridentate dipicolinate ligands *via* their carboxylate and nitrogen donors. Nevertheless, the Ni–N and Ni–O bond lengths in the two ligands are different: Ni1–N1 = 1.974 (3) Å and Ni1–N2 = 1.962 (3) Å; Ni1–O11 and Ni1–O14 = 2.164 (3) and 2.179 (3) Å, while Ni1–O24 and Ni1–O21 = 2.159 (3) and 2.098 (3) Å, respectively. The planes defining the rings are orthogonal to each other. Atom Ni2 is octahedrally coordinated by five H₂O molecules together with one O atom from one dipicolinate coordinated to Ni1, leading to the dinuclear structure. Furthermore, there are two water molecules in the asymmetric unit (Fig. 1 and Table 2).

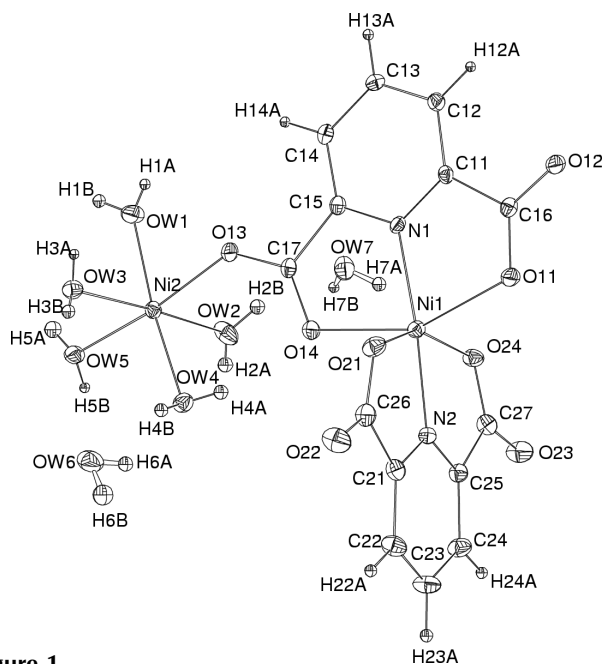


Figure 1
The molecular structure of (I), showing 10% displacement ellipsoids for non-H atoms.

Experimental

The title compound, (I), was prepared by mixing hot ethanol-water (3:2, v/v, 25 ml) solutions of nickel iodide (0.157 g, 0.5 mmol) and dipicolinic acid (0.077 g, 0.5 mmol), and stirring at 353 K for 30 min. 1,10-Phenanthroline (0.090 g, 0.5 mmol) was added and the resulting mixture stirred for 1.5 h and then filtered. After allowing the solution to stand for 1 month, light-green single crystals formed.

Crystal data

$[\text{Ni}_2(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$
 $M_r = 573.74$
 Monoclinic, $P2_1/c$
 $a = 8.3399$ (2) Å
 $b = 27.2748$ (6) Å
 $c = 9.6593$ (1) Å
 $\beta = 98.588$ (1)°
 $V = 2172.56$ (7) Å³
 $Z = 4$

$D_x = 1.754$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4506 reflections
 $\theta = 1.5\text{--}25.0^\circ$
 $\mu = 1.81$ mm⁻¹
 $T = 293$ (2) K
 Prism, green
 $0.48 \times 0.36 \times 0.34$ mm

Data collection

Siemens SMART CCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.408$, $T_{\max} = 0.540$
 6851 measured reflections

3767 independent reflections
 3290 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -8 \rightarrow 9$
 $k = -32 \rightarrow 20$
 $l = -11 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.112$
 $S = 0.95$
 3767 reflections
 355 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 7.4039P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.006$
 $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³
 Extinction correction: SHELXTL
 Extinction coefficient: 0.0071 (5)

Table 1

Selected geometric parameters (Å, °).

Ni1—N2	1.962 (3)	Ni2—OW1	2.028 (4)
Ni1—N1	1.974 (3)	Ni2—O13	2.038 (3)
Ni1—O21	2.098 (3)	Ni2—OW2	2.041 (4)
Ni1—O24	2.159 (3)	Ni2—OW5	2.052 (3)
Ni1—O11	2.164 (3)	Ni2—OW4	2.057 (3)
Ni1—O14	2.179 (3)	Ni2—OW3	2.121 (3)
N2—Ni1—N1	174.93 (13)	OW2—Ni2—OW5	92.01 (16)
N2—Ni1—O21	78.42 (13)	OW1—Ni2—OW4	173.37 (16)
N1—Ni1—O21	102.59 (13)	O13—Ni2—OW4	92.05 (13)
N2—Ni1—O24	77.65 (12)	OW2—Ni2—OW4	87.05 (16)
N1—Ni1—O24	101.77 (12)	OW5—Ni2—OW4	95.37 (15)
O21—Ni1—O24	155.33 (12)	OW1—Ni2—OW3	88.70 (17)
N2—Ni1—O11	108.08 (12)	O13—Ni2—OW3	93.99 (13)
N1—Ni1—O11	76.97 (12)	OW2—Ni2—OW3	177.27 (16)
O21—Ni1—O11	86.87 (12)	OW5—Ni2—OW3	85.82 (14)
O24—Ni1—O11	94.90 (12)	OW4—Ni2—OW3	91.50 (15)
N2—Ni1—O14	97.34 (12)	C16—O11—Ni1	113.8 (2)
N1—Ni1—O14	77.64 (12)	C17—O13—Ni2	133.4 (3)
O21—Ni1—O14	95.34 (12)	C17—O14—Ni1	113.0 (2)
O24—Ni1—O14	93.56 (12)	C26—O21—Ni1	114.0 (3)
O11—Ni1—O14	154.38 (11)	C27—O24—Ni1	113.3 (3)
OW1—Ni2—O13	81.33 (15)	C11—N1—Ni1	120.2 (3)
OW1—Ni2—OW2	93.01 (18)	C15—N1—Ni1	119.0 (3)
O13—Ni2—OW2	88.37 (15)	C25—N2—Ni1	120.2 (3)
OW1—Ni2—OW5	91.25 (17)	C21—N2—Ni1	118.3 (3)
O13—Ni2—OW5	172.58 (14)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
OW2—H2B \cdots OW7	0.81 (7)	2.06 (7)	2.837 (5)	161 (7)
OW5—H5B \cdots OW6	0.74 (6)	1.94 (6)	2.655 (6)	162 (6)
OW2—H2A \cdots O22 ⁱ	0.80 (7)	1.92 (7)	2.720 (5)	173 (7)
OW6—H6A \cdots O22 ⁱ	0.72 (8)	2.12 (8)	2.785 (6)	156 (8)
OW1—H1B \cdots O12 ⁱⁱ	0.79 (7)	1.85 (7)	2.633 (5)	171 (7)
OW5—H5A \cdots O11 ⁱⁱ	0.79 (9)	2.01 (9)	2.790 (5)	169 (8)

Symmetry codes: (i) $x, y, z - 1$; (ii) $x - 1, y, z - 1$.

The water H atoms were refined, while the remaining H atoms were located geometrically and refined with constraints. The O—H bond lengths are in the range 0.64 (6)–0.96 (11) Å.

Data collection: SMART (Siemens, 1996); cell refinement: SMART and SAINT (Siemens, 1994); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Siemens, 1994); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXL97 (Sheldrick, 1997).

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