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catena-Poly[[[diaquanickel(II)]-μ-pyridine-2,4-dicarboxylato-[tetraaquanickel(II)]-μ-pyridine-2,4-dicarboxylato] dihydrate]

Yen-Hsiang Liu* and Pei-Ci Jhang

Department of Chemistry, Fu Jen Catholic University, Hsinchuang, Taipei County, Taiwan
Correspondence e-mail: chem2022@mails.fju.edu.tw

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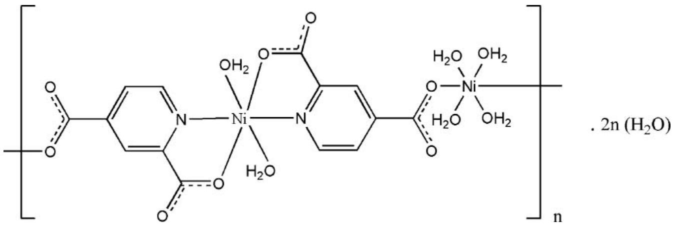
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.036; wR factor = 0.092; data-to-parameter ratio = 11.8.

The asymmetric unit of the title coordination polymer, $\{[Ni_2(C_7H_3O_4N)_2(H_2O)_6]\cdot 2H_2O\}_n$, contains two crystallographically distinct Ni^{II} cations, located on inversion centres. One of the Ni ions exists in an octahedral coordination environment formed by two water molecules and two pyridinecarboxylate dianions that serve as N,O-donors. The other Ni ion is coordinated by four water molecules and two monodentate pyridinecarboxylate dianions with an octahedral geometry. The deprotonated pyridine-2,4-dicarboxylic acid (pdc^{2-}) ligand bridges Ni^{II} ions to form the one-dimensional coordination polymer. Extensive hydrogen bonding helps to stabilize the crystal structure.

Related literature

For related literature, see: Kitagawa *et al.* (2004); Yaghi *et al.* (2003).



Experimental

Crystal data

$[Ni_2(C_7H_3O_4N)_2(H_2O)_6]\cdot 2H_2O$
M_r = 591.76
Triclinic, $P\overline{1}$
a = 5.2115 (12) Å
b = 8.4001 (18) Å
c = 13.107 (3) Å
α = 105.130 (17)°
β = 95.953 (18)°
γ = 101.584 (17)°
V = 535.2 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.85 mm^{-1}
T = 298 (2) K
0.25 × 0.15 × 0.10 mm

Data collection

Bruker P4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.706, T_{max} = 0.825
2075 measured reflections
1854 independent reflections
1354 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
3 standard reflections every 97 reflections intensity decay: 1.0%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.092
S = 1.01
1854 reflections
157 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni1—O1	2.055 (3)	Ni2—O3	2.074 (3)
Ni1—N1	2.063 (3)	Ni2—O22	2.039 (3)
Ni1—O21	2.099 (3)	Ni2—O23	2.048 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O21—H21A···O4^{i}	0.84	1.90	2.740 (4)	173
O21—H21B···O1^{ii}	0.84	1.93	2.763 (4)	172
O22—H22A···O31	0.82	2.02	2.767 (4)	151
O22—H22B···O23^{iii}	0.84	1.98	2.807 (4)	171
O23—H23A···O2^{iv}	0.84	1.86	2.701 (4)	173
O23—H23B···O4^{v}	0.83	1.82	2.644 (4)	168
O31—H31A···O2	0.84	1.96	2.775 (4)	164
O31—H31B···O31^{iv}	0.84	2.35	3.030 (8)	139

Symmetry codes: (i) $x, y+1, z$; (ii) $x+1, y, z$; (iii) $x-1, y, z$; (iv) $-x, -y-1, -z$; (v) $-x+1, -y-2, -z$.

Data collection: *XSCANS* (Bruker, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2253).

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supplementary materials

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catena-Poly[[[diaquanickel(II)]-μ-pyridine-2,4-dicarboxylato-[tetraaquanickel(II)]-μ-pyridine-2,4-dicarboxylato] dihydrate]

Y.-H. Liu and **P.-C. Jhang**

Comment

The use of multifunctional organic ligands such as 4,4'-bipyridine and 1,4-benzenedicarboxylic acid have been recognized as an efficient N, O donors toward the assembly of metal-organic coordination polymers (Kitagawa *et al.*, 2004; Yaghi *et al.*, 2003). Herein we demonstrate that a multifunctional bridging ligand, pyridine-2,4-dicarboxylic acid, not only serves as an efficient N, O donor ligand, but also exhibits versatile non-covalent interactions (*e.g.* hydrogen-bonding and π-π stacking interactions) towards the assembly of supramolecular coordination networks.

The asymmetric unit of (**I**) (Fig. 1) consists of two crystallographically distinct Ni^{II} cations, and both of the Ni^{II} ions exist in crystallographic inversion centers with site occupation factor of 0.5. The Ni1 ion exists in an octahedral coordination environment that is coordinated by two water molecules, and chelated by two pyridinecarboxylate groups that serve as N, O donors. The Ni1—O distances are 2.054 (3) Å and 2.099 (3) Å, and Ni—N distance is 2.063 (3) Å. The Ni2 ion is coordinated by four water molecules as well as two monodentate carboxylate groups to form an octahedral coordination environment. The Ni2—O distances range from 2.039 (3) to 2.074 (3) Å. The asymmetric unit consists of one deprotonated pyridine-2,4-dicarboxylic acid (H_2pdc) ligand. The observation of symmetrical carbon–oxygen bond lengths of 1.246 (4)/ 1.269 (4) Å and 1.245 (5)/1.249 (5) Å of the carboxyl groups reveals that the H_2pdc ligand is deprotonated to become pdc^{2-} anion. One lattice water molecule is also revealed from the difference Fourier map. Therefore, the formula of (**I**) become $[Ni(C_7H_3O_4N)(H_2O)_3{\cdot}H_2O]_n$. The Ni^{ii} cations are connected by the pdc^{2-} ligands to form one-dimensional chains (Fig. 2). There are π-π stacking interactions of the parallel 1-D chains. The distance between the pyridinedicarboxylate ligands of the neighboring parallel chains is about 3.23 Å. These 1-D chains also engage hydrogen-bonding interactions among themselves as well as lattice water molecules to result in a three-dimensional supramolecular network.

Experimental

All reagents and solvents were used as obtained without further purification. $Ni(NO_3)_2{\cdot}6H_2O$ (1.0 mmol), pyridine-2,4-dicarboxylic acid (1.0 mmol) were dissolved in 5 ml benzyl alcohol and 5 ml distilled water. The mixture was sealed in a Teflon-lined stainless steel vessel and held at 413 K for 96 h. The vessel was gradually cooled to room temperature, and green crystals of (**I**) suitable for crystallographic analysis were obtained.

Refinement

The C-bound H atoms were placed in calculated positions (C—H = 0.93 Å) and refined in the riding-model approximation with *U*iso(H) = 1.2 *U*eq(C). Water H atoms were located in a difference Fourier map, and refined as riding model with O—H distances range from 0.82 to 0.84 Å, and with *U*iso(H) = 1.5*U*eq(O). Due to the uncertainty in the assignment of one of the H atom (H31B) of the slightly disordered lattice water molecule (O31) from the difference Fourier map, its position is only approximate. No attempt was made to resolve the disordered nature of the lattice water molecule (O31). Diffraction data with 2θ angle higher than 50° were not collected due to the weakly diffracted crystal sample of (**I**).

Figures

Fig. 1. The asymmetric unit, expanded to show the complete coordination of the Ni^{ii} cations, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) 1 − *x*, −*y*, 1 − *z*; (ii) −*x*, −2 − *y*, −*z*].

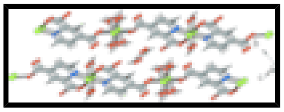

Fig. 2. Solid-state packing diagram of the one-dimensional coordination polymer of (**I**).

catena-Poly[[[diaquanickel(II)]-μ-pyridine-2,4-dicarboxylato- [tetraaquanickel(II)]-μ-pyridine-2,4-dicarboxylato] dihydrate]

Crystal data

$[Ni_2(C_7H_3O_4N)_2(H_2O)_6]\cdot 2H_2O$	$Z = 1$
$M_r = 591.76$	$F_{000} = 304$
Triclinic, $P\overline{1}$	$D_x = 1.836$ Mg m^{-3}
Hall symbol: -P 1	Mo *K*α radiation λ = 0.71073 Å
a = 5.2115 (12) Å	Cell parameters from 23 reflections
b = 8.4001 (18) Å	θ = 8.1–12.5°
c = 13.107 (3) Å	μ = 1.85 mm^{-1}
α = 105.130 (17)°	*T* = 298 (2) K
β = 95.953 (18)°	Block, green
γ = 101.584 (17)°	0.25 × 0.15 × 0.10 mm
V = 535.2 (2) Å^3	

Data collection

Bruker P4 diffractometer	$R_{int} = 0.032$
Radiation source: sealed tube	$\theta_{max} = 25.0°$
Monochromator: graphite	$\theta_{min} = 2.5°$
T = 298 K	*h* = 0→6
2θ/ω scans	*k* = −9→9
Absorption correction: ψ scan (North *et al.*, 1968)	*l* = −14→14
$T_{min} = 0.706$, $T_{max} = 0.825$	3 standard reflections
2075 measured reflections	every 97 reflections
1854 independent reflections	intensity decay: 1.0%
1354 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	157 parameters
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.0365P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.092$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.01$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
1854 reflections	$\Delta\rho_{min} = -0.35$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Ni1	0.5	0	0.5	0.0203 (2)
Ni2	0	−1	0	0.0244 (2)
N1	0.4972 (6)	−0.2439 (3)	0.4134 (2)	0.0224 (7)
O1	0.1785 (5)	−0.0429 (3)	0.3831 (2)	0.0257 (6)
O2	−0.0586 (6)	−0.2348 (3)	0.2359 (2)	0.0313 (7)
O3	0.2226 (6)	−0.7857 (3)	0.1175 (2)	0.0345 (7)
O4	0.5387 (6)	−0.8362 (3)	0.2244 (2)	0.0394 (8)
O21	0.7520 (5)	0.1049 (3)	0.4072 (2)	0.0286 (6)
H21A	0.6818	0.1136	0.3489	0.043*
H21B	0.8732	0.0544	0.394	0.043*
O22	−0.2250 (6)	−0.8384 (3)	−0.0278 (2)	0.0380 (7)
H22A	−0.1825	−0.7389	0.009	0.057*
H22B	−0.3828	−0.869	−0.0589	0.057*
O23	0.2292 (5)	−0.9432 (3)	−0.1094 (2)	0.0308 (7)
H23A	0.1703	−0.8958	−0.1529	0.046*
H23B	0.2827	−1.0225	−0.1464	0.046*
O31	−0.2487 (8)	−0.5032 (4)	0.0507 (3)	0.0678 (11)
H31A	−0.2158	−0.4143	0.1023	0.102*
H31B	−0.158	−0.4738	0.0066	0.102*
C1	0.1279 (7)	−0.1862 (4)	0.3130 (3)	0.0216 (8)
C2	0.3949 (8)	−0.7462 (5)	0.1992 (3)	0.0262 (9)
C3	0.3027 (7)	−0.3048 (4)	0.3267 (3)	0.0205 (8)
C4	0.2634 (8)	−0.4659 (4)	0.2571 (3)	0.0245 (8)
H4	0.1278	−0.5048	0.1982	0.029*
C5	0.4299 (7)	−0.5695 (4)	0.2765 (3)	0.0229 (8)
C6	0.6267 (7)	−0.5059 (4)	0.3655 (3)	0.0243 (8)

H6	0.7405	−0.572	0.3808	0.029*
C7	0.6542 (8)	−0.3444 (4)	0.4317 (3)	0.0249 (8)
H7	0.7874	−0.3037	0.4915	0.03*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0228 (4)	0.0160 (3)	0.0175 (4)	0.0077 (3)	−0.0027 (3)	−0.0030 (3)
Ni2	0.0279 (4)	0.0193 (4)	0.0206 (4)	0.0088 (3)	−0.0037 (3)	−0.0032 (3)
N1	0.0257 (17)	0.0184 (15)	0.0213 (16)	0.0083 (13)	0.0008 (13)	0.0018 (12)
O1	0.0295 (15)	0.0183 (13)	0.0243 (14)	0.0105 (11)	−0.0031 (12)	−0.0035 (11)
O2	0.0352 (16)	0.0256 (14)	0.0266 (15)	0.0110 (12)	−0.0114 (13)	−0.0003 (12)
O3	0.0386 (17)	0.0243 (14)	0.0298 (16)	0.0104 (13)	−0.0100 (13)	−0.0067 (12)
O4	0.062 (2)	0.0324 (15)	0.0255 (15)	0.0318 (15)	−0.0015 (15)	−0.0012 (12)
O21	0.0296 (16)	0.0331 (15)	0.0248 (14)	0.0158 (12)	0.0013 (12)	0.0063 (12)
O22	0.0363 (17)	0.0236 (14)	0.0459 (18)	0.0116 (13)	−0.0092 (14)	−0.0013 (13)
O23	0.0411 (17)	0.0282 (14)	0.0257 (15)	0.0192 (13)	0.0039 (13)	0.0045 (11)
O31	0.087 (3)	0.0428 (19)	0.053 (2)	0.017 (2)	−0.013 (2)	−0.0136 (17)
C1	0.023 (2)	0.0219 (19)	0.0178 (19)	0.0067 (16)	−0.0017 (16)	0.0036 (15)
C2	0.032 (2)	0.024 (2)	0.022 (2)	0.0105 (18)	0.0044 (18)	0.0012 (16)
C3	0.0208 (19)	0.0184 (18)	0.0192 (18)	0.0050 (15)	−0.0008 (15)	0.0014 (14)
C4	0.026 (2)	0.022 (2)	0.0200 (18)	0.0080 (18)	−0.0057 (15)	−0.0029 (16)
C5	0.027 (2)	0.0190 (18)	0.0195 (18)	0.0068 (16)	0.0007 (16)	−0.0003 (15)
C6	0.026 (2)	0.0230 (19)	0.023 (2)	0.0110 (16)	−0.0021 (16)	0.0034 (15)
C7	0.026 (2)	0.0228 (19)	0.0189 (19)	0.0060 (16)	−0.0078 (16)	−0.0021 (15)

Geometric parameters (Å, °)

Ni1—O1	2.055 (3)	O21—H21A	0.8399
Ni1—O1^{i}	2.055 (3)	O21—H21B	0.8377
Ni1—N1	2.063 (3)	O22—H22A	0.8202
Ni1—N1^{i}	2.063 (3)	O22—H22B	0.8369
Ni1—O21	2.099 (3)	O23—H23A	0.8426
Ni1—O21^{i}	2.099 (3)	O23—H23B	0.8312
Ni2—O3^{ii}	2.074 (3)	O31—H31A	0.8395
Ni2—O3	2.074 (3)	O31—H31B	0.8387
Ni2—O22	2.039 (3)	C1—C3	1.510 (5)
Ni2—O22^{ii}	2.039 (3)	C2—C5	1.526 (5)
Ni2—O23	2.048 (3)	C3—C4	1.382 (5)
Ni2—O23^{ii}	2.048 (3)	C4—C5	1.396 (5)
N1—C7	1.335 (5)	C4—H4	0.93
N1—C3	1.353 (5)	C5—C6	1.380 (5)
O1—C1	1.268 (4)	C6—C7	1.377 (5)
O2—C1	1.247 (4)	C6—H6	0.93
O3—C2	1.249 (5)	C7—H7	0.93
O4—C2	1.245 (5)		
O1—Ni1—O1^{i}	180.0000 (10)	C1—O1—Ni1	114.8 (2)

O1—Ni1—N1	80.69 (11)	C2—O3—Ni2	139.8 (3)
O1^{i}—Ni1—N1	99.31 (11)	Ni1—O21—H21A	117.6
O1—Ni1—N1^{i}	99.31 (11)	Ni1—O21—H21B	112.6
O1^{i}—Ni1—N1^{i}	80.69 (11)	H21A—O21—H21B	107.2
N1—Ni1—N1^{i}	180.00 (16)	Ni2—O22—H22A	119
O1—Ni1—O21	90.36 (11)	Ni2—O22—H22B	124.5
O1^{i}—Ni1—O21	89.64 (11)	H22A—O22—H22B	113.4
N1—Ni1—O21	91.84 (11)	Ni2—O23—H23A	118.4
N1^{i}—Ni1—O21	88.16 (11)	Ni2—O23—H23B	116.4
O1—Ni1—O21^{i}	89.64 (11)	H23A—O23—H23B	105.3
O1^{i}—Ni1—O21^{i}	90.36 (11)	H31A—O31—H31B	103
N1—Ni1—O21^{i}	88.16 (11)	O2—C1—O1	124.0 (3)
N1^{i}—Ni1—O21^{i}	91.84 (11)	O2—C1—C3	118.9 (3)
O21—Ni1—O21^{i}	180	O1—C1—C3	117.0 (3)
O22—Ni2—O22^{ii}	180.0000 (10)	O4—C2—O3	126.8 (3)
O22—Ni2—O23	90.28 (11)	O4—C2—C5	116.9 (3)
O22^{ii}—Ni2—O23	89.72 (11)	O3—C2—C5	116.3 (3)
O22—Ni2—O23^{ii}	89.72 (11)	N1—C3—C4	122.2 (3)
O22^{ii}—Ni2—O23^{ii}	90.28 (11)	N1—C3—C1	115.3 (3)
O23—Ni2—O23^{ii}	180	C4—C3—C1	122.5 (3)
O22—Ni2—O3^{ii}	96.62 (11)	C3—C4—C5	119.1 (3)
O22^{ii}—Ni2—O3^{ii}	83.38 (11)	C3—C4—H4	120.4
O23—Ni2—O3^{ii}	89.44 (12)	C5—C4—H4	120.4
O23^{ii}—Ni2—O3^{ii}	90.56 (12)	C6—C5—C4	118.0 (3)
O22—Ni2—O3	83.38 (11)	C6—C5—C2	121.9 (3)
O22^{ii}—Ni2—O3	96.62 (11)	C4—C5—C2	120.1 (3)
O23—Ni2—O3	90.56 (12)	C7—C6—C5	119.8 (3)
O23^{ii}—Ni2—O3	89.44 (11)	C7—C6—H6	120.1
O3^{ii}—Ni2—O3	180	C5—C6—H6	120.1
C7—N1—C3	118.2 (3)	N1—C7—C6	122.6 (3)
C7—N1—Ni1	129.6 (2)	N1—C7—H7	118.7
C3—N1—Ni1	112.2 (2)	C6—C7—H7	118.7

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) −*x*, −*y*−2, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O21—H21A···O4^{iii}	0.84	1.90	2.740 (4)	173
O21—H21B···O1^{iv}	0.84	1.93	2.763 (4)	172
O22—H22A···O31	0.82	2.02	2.767 (4)	151
O22—H22B···O23^{v}	0.84	1.98	2.807 (4)	171
O23—H23A···O2^{vi}	0.84	1.86	2.701 (4)	173
O23—H23B···O4^{vii}	0.83	1.82	2.644 (4)	168

O31—H31A···O2	0.84	1.96	2.775 (4)	164
O31—H31B···O31$^{\text{vi}}$	0.84	2.35	3.030 (8)	139

Symmetry codes: (iii) *x*, *y*+1, *z*; (iv) *x*+1, *y*, *z*; (v) *x*−1, *y*, *z*; (vi) −*x*, −*y*−1, −*z*; (vii) −*x*+1, −*y*−2, −*z*.

Fig. 1

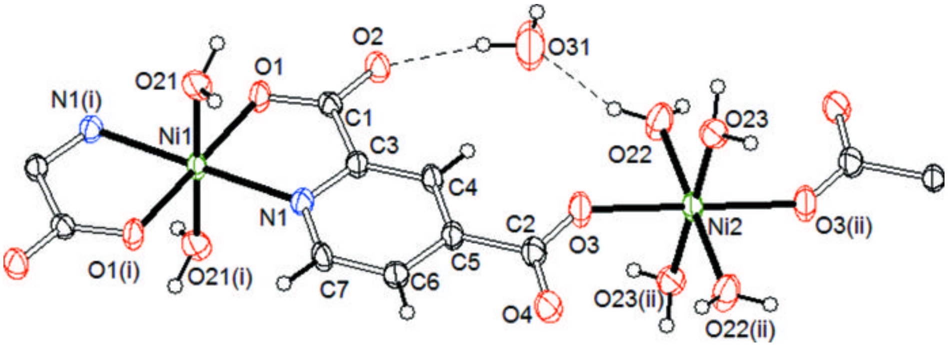
O2
O31
O21
O1
N1(i)
Ni1
C1
C3
O22
O23
C4
N1
C2
O3
Ni2
O3(ii)
C5
O1(i)
O21(i)
C7
C6
O23(ii)
O4
O22(ii)

Fig. 2