

## Diaqua(2,2'-bipyridine-6,6'-dicarboxylato)nickel(II)

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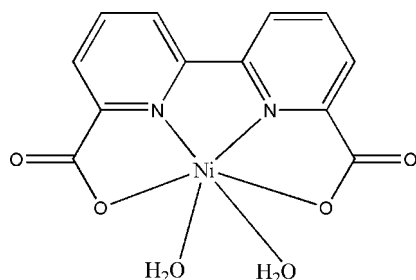
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 Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.032;  $wR$  factor = 0.082; data-to-parameter ratio = 12.5.

In the title compound,  $[\text{Ni}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]$ , the  $\text{Ni}^{\text{II}}$  atom (site symmetry 2) displays a distorted *cis*- $\text{NiN}_2\text{O}_4$  octahedral coordination geometry with two N atoms and two O atoms of the tetradentate 2,2'-bipyridine-6,6'-dicarboxylate ligand in the equatorial plane and two water molecules in axial positions. The complete dianionic ligand is generated by crystallographic twofold symmetry. In the crystal, a two-dimensional supramolecular structure parallel to (001) is formed through  $\text{O}-\text{H}\cdots\text{O}$  hydrogen-bond interactions between the coordinated water molecules and the O atoms of nearby carboxylate groups.

### Related literature

For transition metal complexes with the title ligand, see: Knight *et al.* (2006); Duan *et al.* (2009); Wang *et al.* (2009). For lanthanide metal complexes with the title ligand, see: Bunzli *et al.* (2000); Wang *et al.* (2010).



### Experimental

#### Crystal data

$[\text{Ni}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]$	$V = 1237.8$ (3) Å <sup>3</sup>
$M_r = 336.93$	$Z = 4$
Orthorhombic, <i>Pccn</i>	Mo $K\alpha$ radiation
$a = 7.1056$ (9) Å	$\mu = 1.60$ mm <sup>-1</sup>
$b = 11.3608$ (15) Å	$T = 296$ K
$c = 15.3334$ (19) Å	$0.24 \times 0.16 \times 0.10$ mm

#### Data collection

Bruker APEXII CCD diffractometer	6269 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2005)	1274 independent reflections
$T_{\text{min}} = 0.766$ , $T_{\text{max}} = 0.857$	1098 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.082$	$\Delta\rho_{\text{max}} = 0.48$ e Å <sup>-3</sup>
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.23$ e Å <sup>-3</sup>
1274 reflections	
102 parameters	
2 restraints	

**Table 1**

Selected bond lengths (Å).

Ni1—N1	1.9975 (19)	Ni1—O1	2.1335 (16)
Ni1—O3	2.0553 (18)		

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H3A}\cdots\text{O2}^{\text{i}}$	0.81 (2)	1.90 (2)	2.708 (2)	176 (3)
$\text{O3}-\text{H3B}\cdots\text{O2}^{\text{ii}}$	0.83 (2)	1.95 (2)	2.772 (3)	172 (3)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5864).

### References

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**supplementary materials**

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## Diaqua(2,2'-bipyridine-6,6'-dicarboxylato)nickel(II)

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### Comment

Pyridyl carboxylic acid is an important class of organic ligands and has been widely used in coordination chemistry. 2,2'-Bipyridine-6,6'-dicarboxylate ligand is coordinated with transition metal (Duan *et al.*, 2009; Knight *et al.*, 2006 and Wang *et al.*, 2009) and lanthanide metal ions (Bunzli *et al.*, 2000 and Wang *et al.*, 2010). Herein, we report crystal structure of a new nickel complex with 2,2'-bipyridine-6,6'-dicarboxylate ligand.

The atom-numbering scheme of (I) is shown in Fig. 1. The Ni<sup>II</sup> atom displays a distorted octahedral coordination geometry with two N atoms and two O atoms of 2,2'-bipyridine-6,6'-dicarboxylate in equatorial plane and two water molecules in apical positions. A two-dimensional supramolecular structure is formed through hydrogen interactions between the oxygen atoms of coordination water molecules and the oxygen atoms of carboxylate groups [O3—H3A...O2<sup>i</sup>, 2.708 (3) Å, 176 (3)°, symmetric code i: (-x - 1/2, -y + 3/2, z); O3—H3B...O2<sup>ii</sup>, 2.772 (3) Å, 172 (3)°, symmetric code ii: (-x, y - 1/2, -z + 1/2)].

### Experimental

The title compound was prepared by the reaction of Ni(NO<sub>3</sub>)<sub>2</sub> with 2,2'-bipyridine-6,6'-dicarboxylic acid (H<sub>2</sub>bpdc) in a water solution. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2 mmol) and H<sub>2</sub>bpdc (0.2 mmol) were dissolved in 25 ml deionized water and adjusted the pH to 7 with 0.05 mol L<sup>-1</sup> NaOH aqueous solution. After one week, green blocks were obtained. Elemental analysis for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>NiO<sub>6</sub> calculated: C 42.78, H 2.99, N 8.32%; found: C 42.57, H 2.89, N 8.46%.

### Refinement

The water H atoms were located in a difference Fourier map and refined with restrained O—H bond lengths [0.85 (2) Å] and fixed isotropic displacement parameters ( $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{O})$ ). The carbon H atoms were placed at calculated positions (C—H = 0.93–0.96 Å) and refined as riding model with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{carrier})$ .

### Figures

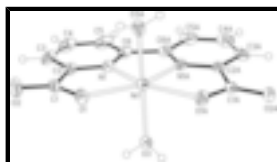


Fig. 1. The molecular structure of (I), showing 30% probability displacement ellipsoids. Atoms labelled with the suffix A are at the symmetry position (-x + 1/2, -y + 3/2, z).

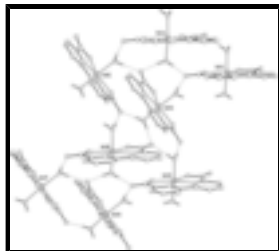


Fig. 2. View of a two-dimensional supramolecular structure constructed through hydrogen bonding interactions in (I). Hydrogen atoms of carbon atoms have been omitted for clarity.

## Diaqua(2,2'-bipyridine-6,6'-dicarboxylato)nickel(II)

### Crystal data

[Ni(C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>]

$M_r = 336.93$

Orthorhombic, *Pccn*

Hall symbol: -P 2ab 2ac

$a = 7.1056$  (9) Å

$b = 11.3608$  (15) Å

$c = 15.3334$  (19) Å

$V = 1237.8$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 688$

$D_x = 1.808$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1650 reflections

$\theta = 3.2\text{--}25.2^\circ$

$\mu = 1.60$  mm<sup>-1</sup>

$T = 296$  K

Block, green

$0.24 \times 0.16 \times 0.10$  mm

### Data collection

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2005)

$T_{\min} = 0.766$ ,  $T_{\max} = 0.857$

6269 measured reflections

1274 independent reflections

1098 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 26.4^\circ$ ,  $\theta_{\min} = 2.7^\circ$

$h = -8 \rightarrow 8$

$k = -13 \rightarrow 14$

$l = -10 \rightarrow 19$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.082$

$S = 1.06$

1274 reflections

102 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.5888P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.48$  e Å<sup>-3</sup>

2 restraints

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

*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.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.2500	0.7500	0.16327 (3)	0.02540 (16)
N1	0.0931 (3)	0.80137 (16)	0.06211 (12)	0.0285 (4)
O1	0.0167 (2)	0.83346 (15)	0.22531 (11)	0.0360 (4)
O2	-0.2446 (2)	0.93408 (18)	0.19595 (16)	0.0517 (6)
C1	-0.1035 (3)	0.8756 (2)	0.17424 (18)	0.0348 (6)
C2	-0.0683 (4)	0.8569 (2)	0.07707 (17)	0.0332 (6)
C3	-0.1808 (4)	0.8936 (2)	0.0083 (2)	0.0464 (7)
H3	-0.2934	0.9332	0.0182	0.056*
C4	-0.1204 (5)	0.8695 (3)	-0.0750 (2)	0.0563 (9)
H4	-0.1951	0.8915	-0.1221	0.068*
C5	0.0486 (5)	0.8132 (2)	-0.09017 (18)	0.0506 (8)
H5	0.0894	0.7982	-0.1467	0.061*
C6	0.1564 (4)	0.7796 (2)	-0.01856 (16)	0.0348 (6)
O3	0.1216 (2)	0.58888 (16)	0.17647 (13)	0.0380 (5)
H3A	0.009 (3)	0.584 (3)	0.1803 (18)	0.046*
H3B	0.169 (4)	0.545 (2)	0.2135 (15)	0.046*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.0254 (3)	0.0293 (3)	0.0215 (2)	0.00250 (16)	0.000	0.000
N1	0.0341 (11)	0.0256 (10)	0.0260 (11)	-0.0004 (9)	-0.0053 (9)	-0.0005 (8)
O1	0.0336 (9)	0.0402 (10)	0.0343 (10)	0.0040 (8)	0.0046 (8)	-0.0040 (8)
O2	0.0263 (10)	0.0466 (12)	0.0821 (15)	0.0055 (8)	-0.0004 (9)	-0.0232 (11)
C1	0.0248 (12)	0.0269 (12)	0.0526 (17)	-0.0047 (10)	0.0005 (12)	-0.0078 (11)
C2	0.0316 (13)	0.0217 (12)	0.0464 (16)	-0.0021 (10)	-0.0109 (11)	-0.0021 (10)
C3	0.0437 (15)	0.0291 (14)	0.067 (2)	-0.0016 (11)	-0.0276 (15)	0.0050 (13)
C4	0.073 (2)	0.0378 (16)	0.059 (2)	-0.0073 (15)	-0.0407 (18)	0.0134 (14)
C5	0.085 (2)	0.0380 (16)	0.0289 (15)	-0.0094 (16)	-0.0177 (15)	0.0061 (11)
C6	0.0530 (17)	0.0261 (12)	0.0252 (12)	-0.0045 (11)	-0.0073 (12)	0.0018 (9)
O3	0.0259 (9)	0.0364 (10)	0.0519 (12)	0.0001 (8)	0.0044 (9)	0.0117 (8)

## supplementary materials

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### Geometric parameters (Å, °)

Ni1—Ni <sup>i</sup>	1.9975 (19)	C2—C3	1.387 (4)
Ni1—N1	1.9975 (19)	C3—C4	1.375 (5)
Ni1—O3 <sup>i</sup>	2.0553 (18)	C3—H3	0.9300
Ni1—O3	2.0553 (18)	C4—C5	1.381 (5)
Ni1—O1 <sup>i</sup>	2.1335 (16)	C4—H4	0.9300
Ni1—O1	2.1335 (16)	C5—C6	1.392 (4)
N1—C2	1.329 (3)	C5—H5	0.9300
N1—C6	1.339 (3)	C6—C6 <sup>i</sup>	1.491 (5)
O1—C1	1.254 (3)	O3—H3A	0.806 (18)
O2—C1	1.247 (3)	O3—H3B	0.827 (17)
C1—C2	1.526 (4)		
N1 <sup>i</sup> —Ni1—N1	78.11 (11)	O2—C1—C2	117.8 (2)
N1 <sup>i</sup> —Ni1—O3 <sup>i</sup>	95.10 (8)	O1—C1—C2	116.4 (2)
N1—Ni1—O3 <sup>i</sup>	93.67 (8)	N1—C2—C3	120.6 (3)
N1 <sup>i</sup> —Ni1—O3	93.67 (8)	N1—C2—C1	112.1 (2)
N1—Ni1—O3	95.10 (8)	C3—C2—C1	127.3 (3)
O3 <sup>i</sup> —Ni1—O3	168.70 (11)	C4—C3—C2	117.8 (3)
N1 <sup>i</sup> —Ni1—O1 <sup>i</sup>	77.45 (7)	C4—C3—H3	121.1
N1—Ni1—O1 <sup>i</sup>	155.48 (8)	C2—C3—H3	121.1
O3 <sup>i</sup> —Ni1—O1 <sup>i</sup>	90.40 (7)	C3—C4—C5	121.4 (3)
O3—Ni1—O1 <sup>i</sup>	84.56 (7)	C3—C4—H4	119.3
N1 <sup>i</sup> —Ni1—O1	155.48 (8)	C5—C4—H4	119.3
N1—Ni1—O1	77.45 (7)	C4—C5—C6	118.2 (3)
O3 <sup>i</sup> —Ni1—O1	84.56 (7)	C4—C5—H5	120.9
O3—Ni1—O1	90.40 (7)	C6—C5—H5	120.9
O1 <sup>i</sup> —Ni1—O1	127.04 (9)	N1—C6—C5	119.5 (3)
C2—N1—C6	122.5 (2)	N1—C6—C6 <sup>i</sup>	112.53 (14)
C2—N1—Ni1	119.11 (17)	C5—C6—C6 <sup>i</sup>	127.93 (19)
C6—N1—Ni1	118.41 (17)	Ni1—O3—H3A	121 (2)
C1—O1—Ni1	114.88 (15)	Ni1—O3—H3B	115 (2)
O2—C1—O1	125.7 (3)	H3A—O3—H3B	108 (3)
N1 <sup>i</sup> —Ni1—N1—C2	-178.6 (2)	Ni1—N1—C2—C3	-179.86 (17)
O3 <sup>i</sup> —Ni1—N1—C2	-84.19 (18)	C6—N1—C2—C1	-177.4 (2)
O3—Ni1—N1—C2	88.68 (18)	Ni1—N1—C2—C1	1.8 (3)
O1 <sup>i</sup> —Ni1—N1—C2	176.75 (16)	O2—C1—C2—N1	175.2 (2)
O1—Ni1—N1—C2	-0.59 (17)	O1—C1—C2—N1	-2.6 (3)
N1 <sup>i</sup> —Ni1—N1—C6	0.53 (13)	O2—C1—C2—C3	-3.1 (4)
O3 <sup>i</sup> —Ni1—N1—C6	94.98 (18)	O1—C1—C2—C3	179.2 (2)
O3—Ni1—N1—C6	-92.15 (18)	N1—C2—C3—C4	0.6 (4)
O1 <sup>i</sup> —Ni1—N1—C6	-4.1 (3)	C1—C2—C3—C4	178.7 (2)
O1—Ni1—N1—C6	178.57 (19)	C2—C3—C4—C5	-1.5 (4)

N1 <sup>i</sup> —Ni1—O1—C1	3.7 (3)	C3—C4—C5—C6	1.0 (4)
N1—Ni1—O1—C1	-0.96 (16)	C2—N1—C6—C5	-1.6 (4)
O3 <sup>i</sup> —Ni1—O1—C1	94.04 (17)	Ni1—N1—C6—C5	179.24 (19)
O3—Ni1—O1—C1	-96.09 (17)	C2—N1—C6—C6 <sup>i</sup>	177.8 (2)
O1 <sup>i</sup> —Ni1—O1—C1	-179.58 (17)	Ni1—N1—C6—C6 <sup>i</sup>	-1.4 (3)
Ni1—O1—C1—O2	-175.4 (2)	C4—C5—C6—N1	0.6 (4)
Ni1—O1—C1—C2	2.1 (3)	C4—C5—C6—C6 <sup>i</sup>	-178.7 (3)
C6—N1—C2—C3	1.0 (4)		

Symmetry codes: (i)  $-x+1/2, -y+3/2, z$ .

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O3—H3A $\cdots$ O2 <sup>ii</sup>	0.81 (2)	1.90 (2)	2.708 (2)	176 (3)
O3—H3B $\cdots$ O2 <sup>iii</sup>	0.83 (2)	1.95 (2)	2.772 (3)	172 (3)

Symmetry codes: (ii)  $-x-1/2, -y+3/2, z$ ; (iii)  $-x, y-1/2, -z+1/2$ .

Fig. 1

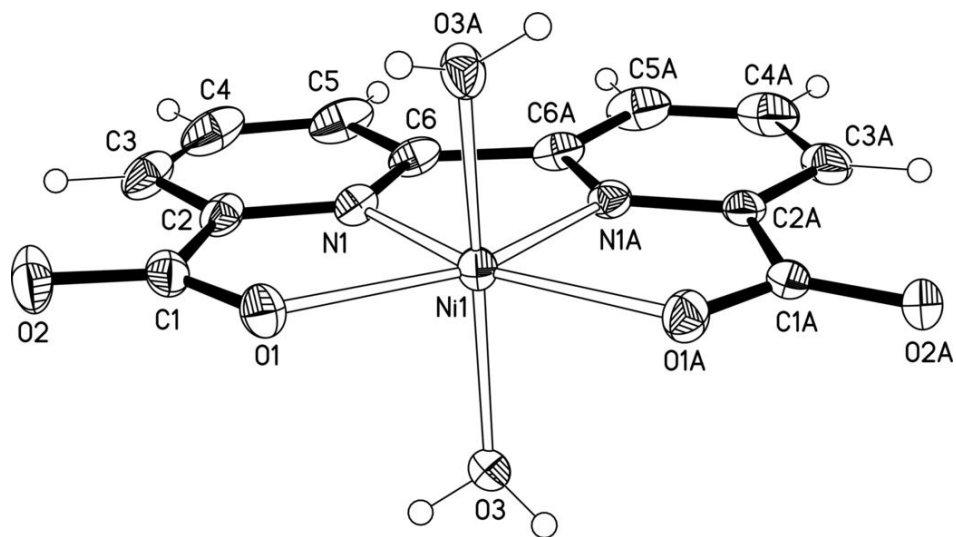




Fig. 2

