metal-organic compounds

Diaqua(2,2′-bipyridine-6,6′-dicarboxylato)nickel(II)

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In the title compound, $[Ni(C_{12}H_6N_2O_4)(H_2O)_2]$, the Ni^{II} atom (site symmetry 2) displays a distorted *cis*-NiN$_2$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 O—H⋯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).
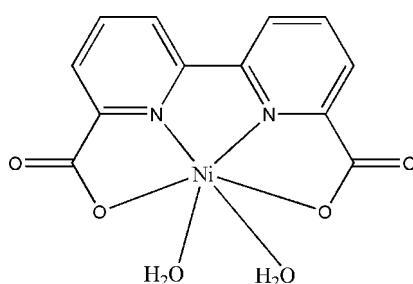
Experimental

Crystal data

$[Ni(C_{12}H_6N_2O_4)(H_2O)_2]$
M_r = 336.93
Orthorhombic, $Pccn$
a = 7.1056 (9) Å
b = 11.3608 (15) Å
c = 15.3334 (19) Å
V = 1237.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.60 mm^{-1}
T = 296 K
$0.24 \times 0.16 \times 0.10$ mm

Data collection

Bruker APEXII CCD diffractometer
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_{int} = 0.036

Refinement

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

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—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3A⋯O2^i	0.81 (2)	1.90 (2)	2.708 (2)	176 (3)
O3—H3B⋯O2^{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).

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supporting information

Diaqua(2,2′-bipyridine-6,6′-dicarboxylato)nickel(II)

Shui Hu, ShiPeng Wen, Huai-Ming Hu and Li Liu

S1. 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 woth 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^{II} 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^i, 2.708 (3) Å, 176 (3) °, symmetric code i: (-x - 1/2, -y + 3/2, z); O3—H3B···O2^{ii}, 2.772 (3) Å, 172 (3) °, symmetric code ii: (-x, y - 1/2, -z + 1/2)].

S2. Experimental

The title compound was prepared by the reaction of Ni(NO$_3$)$_2$ with 2,2′-bipyridine-6,6′-dicarboxylic acid (H$_2$bpdc) in a water solution. Ni(NO$_3$)$_2$.6H$_2$O (0.2 mmol) and H$_2$bpdc (0.2 mmol) were dissolved in 25 ml deionized water and adjusted the pH to 7 with 0.05 mol L^{-1} NaOH aqueous solution. After one week, green blocks were obtained. Elmental analysis for C$_{12}$H$_{10}$N$_2$NiO$_6$ calculated: C 42.78, H 2.99, N 8.32%; found: C 42.57, H 2.89, N 8.46%.

S3. 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_{iso}(H) = 1.2 U_{eq}(O)). The carbon H atoms were placed at calculated positions (C—H = 0.93–0.96 Å) and refined as riding model with U_{iso}(H) = 1.2 U_{eq}(carrier).
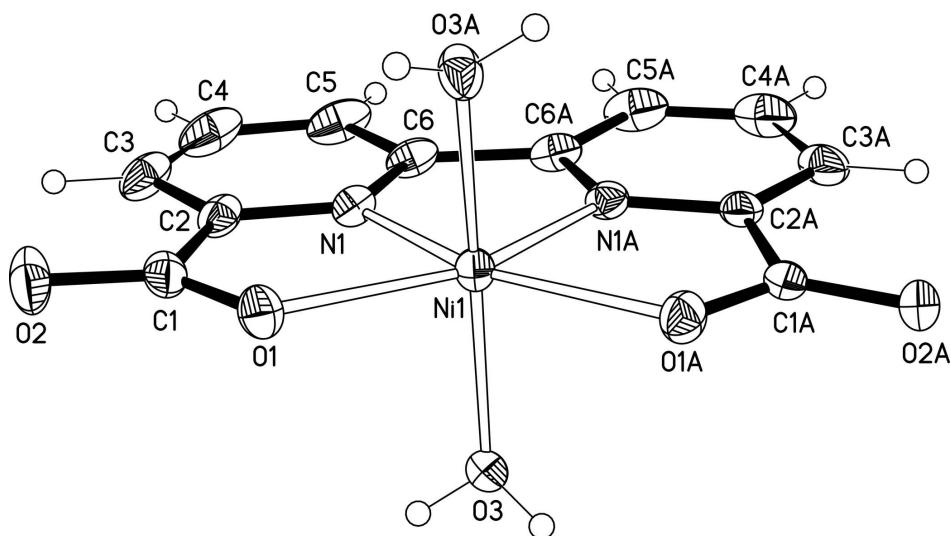
Figure 1

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*).
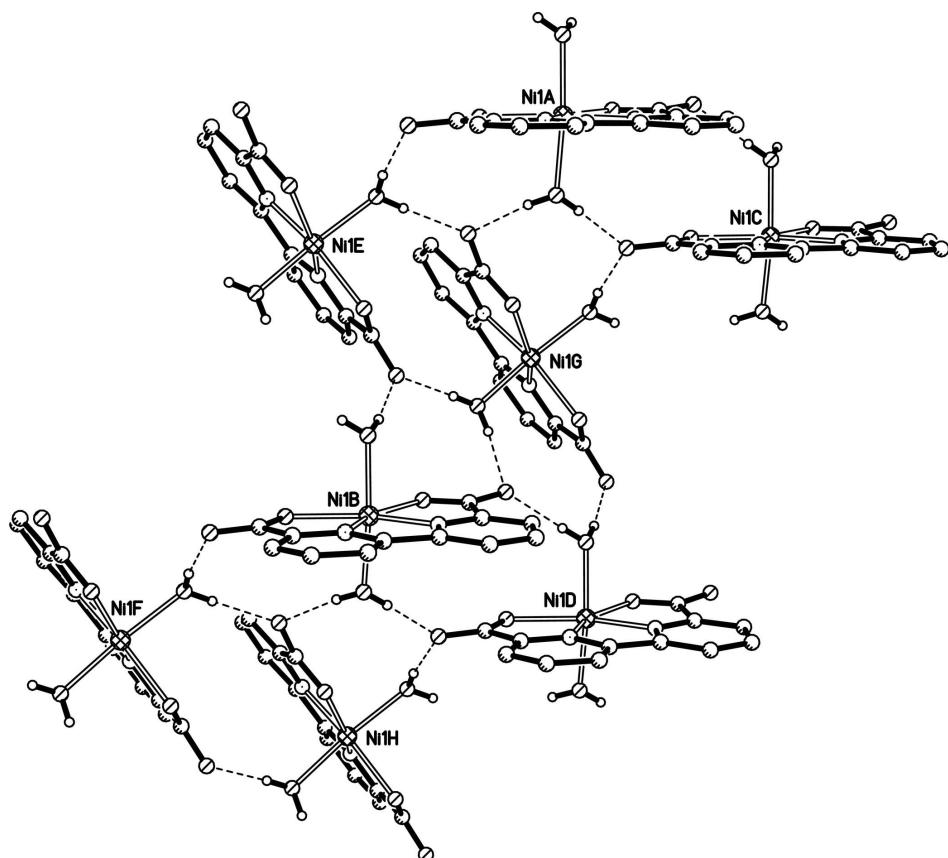
Figure 2

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

$[Ni(C_{12}H_6N_2O_4)(H_2O)_2]$	$F(000) = 688$
$M_r = 336.93$	$D_x = 1.808$ Mg m^{-3}
Orthorhombic, *Pccn*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ab 2ac	Cell parameters from 1650 reflections
$a = 7.1056$ (9) Å	$\theta = 3.2–25.2°$
$b = 11.3608$ (15) Å	$\mu = 1.60$ mm^{-1}
$c = 15.3334$ (19) Å	$T = 296$ K
$V = 1237.8$ (3) Å^3	Block, green
$Z = 4$	$0.24 \times 0.16 \times 0.10$ mm

Data collection

Bruker APEXII CCD diffractometer	6269 measured reflections
Radiation source: fine-focus sealed tube	1274 independent reflections
Graphite monochromator	1098 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.036$
Absorption correction: multi-scan	$\theta_{max} = 26.4°$, $\theta_{min} = 2.7°$
(*SADABS*; Bruker, 2005)	$h = -8 \rightarrow 8$
$T_{min} = 0.766$, $T_{max} = 0.857$	$k = -13 \rightarrow 14$
	$l = -10 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.082$	$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.5888P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	
1274 reflections	
102 parameters	$(\Delta/\sigma)_{max} < 0.001$
2 restraints	$\Delta\rho_{max} = 0.48$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.23$ 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.

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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{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 (Å²)

	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)

Geometric parameters (Å, º)

Ni1—N1[i]	1.9975 (19)	C2—C3	1.387 (4)
Ni1—N1	1.9975 (19)	C3—C4	1.375 (5)
Ni1—O3[i]	2.0553 (18)	C3—H3	0.9300
Ni1—O3	2.0553 (18)	C4—C5	1.381 (5)
Ni1—O1[i]	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[i]	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[i]—Ni1—N1	78.11 (11)	O2—C1—C2	117.8 (2)
N1[i]—Ni1—O3[i]	95.10 (8)	O1—C1—C2	116.4 (2)
N1—Ni1—O3[i]	93.67 (8)	N1—C2—C3	120.6 (3)
N1[i]—Ni1—O3	93.67 (8)	N1—C2—C1	112.1 (2)
N1—Ni1—O3	95.10 (8)	C3—C2—C1	127.3 (3)
O3[i]—Ni1—O3	168.70 (11)	C4—C3—C2	117.8 (3)

N1ⁱ—Ni1—O1ⁱ	77.45 (7)	C4—C3—H3	121.1
N1—Ni1—O1ⁱ	155.48 (8)	C2—C3—H3	121.1
O3ⁱ—Ni1—O1ⁱ	90.40 (7)	C3—C4—C5	121.4 (3)
O3—Ni1—O1ⁱ	84.56 (7)	C3—C4—H4	119.3
N1ⁱ—Ni1—O1	155.48 (8)	C5—C4—H4	119.3
N1—Ni1—O1	77.45 (7)	C4—C5—C6	118.2 (3)
O3ⁱ—Ni1—O1	84.56 (7)	C4—C5—H5	120.9
O3—Ni1—O1	90.40 (7)	C6—C5—H5	120.9
O1ⁱ—Ni1—O1	127.04 (9)	N1—C6—C5	119.5 (3)
C2—N1—C6	122.5 (2)	N1—C6—C6ⁱ	112.53 (14)
C2—N1—Ni1	119.11 (17)	C5—C6—C6ⁱ	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)
N1ⁱ—Ni1—N1—C2	−178.6 (2)	Ni1—N1—C2—C3	−179.86 (17)
O3ⁱ—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)
O1ⁱ—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)
N1ⁱ—Ni1—N1—C6	0.53 (13)	O2—C1—C2—C3	−3.1 (4)
O3ⁱ—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)
O1ⁱ—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)
N1ⁱ—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)
O3ⁱ—Ni1—O1—C1	94.04 (17)	Ni1—N1—C6—C5	179.24 (19)
O3—Ni1—O1—C1	−96.09 (17)	C2—N1—C6—C6ⁱ	177.8 (2)
O1ⁱ—Ni1—O1—C1	−179.58 (17)	Ni1—N1—C6—C6ⁱ	−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—C6ⁱ	−178.7 (3)
C6—N1—C2—C3	1.0 (4)		

Symmetry code: (i) −x+1/2, −y+3/2, z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O2ⁱⁱ	0.81 (2)	1.90 (2)	2.708 (2)	176 (3)
O3—H3B···O2ⁱⁱⁱ	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.