



# Crystal structure of *trans*-diaqua(1,4,8,11-tetraazaundecane)nickel(II) bis(pyridine-2,6-dicarboxylato)nickel(II)

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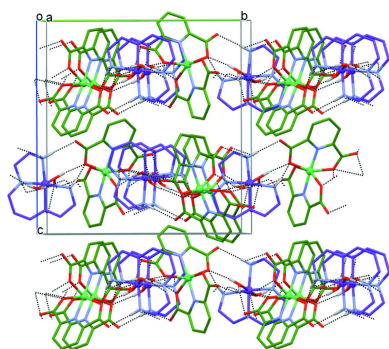
**Supporting information:** this article has supporting information at journals.iucr.org/e

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The asymmetric unit of the title compound, *trans*-diaqua(1,4,8,11-tetraazaundecane- $\kappa^4 N^1, N^4, N^8, N^{11}$ )nickel(II) bis(pyridine-2,6-dicarboxylato- $\kappa^3 O^2, N, O^6$ )-nickel(II)  $\{[\text{Ni}(L)(\text{H}_2\text{O})_2][\text{Ni}(\text{pdc})_2]$  where  $L = 1,4,8,11$ -tetraazaundecane ( $\text{C}_7\text{H}_{20}\text{N}_4$ ) and pdc = the dianion of pyridine-2,6-dicarboxylic acid ( $\text{C}_7\text{H}_3\text{NO}_4^{2-}$ )} consists of an  $[\text{Ni}(L)(\text{H}_2\text{O})_2]^{2+}$  complex cation and a  $[\text{Ni}(\text{pdc})_2]^{2-}$  anion. The metal ion in the cation is coordinated by the four N atoms of the tetraamine ligand and the mutually *trans* O atoms of the water molecules in a tetragonally elongated octahedral geometry with the average equatorial Ni–N bond length slightly shorter than the average axial Ni–O bond [2.087 (4) *versus* 2.128 (4) Å]. The ligand  $L$  adopts its energetically favored conformation with five-membered and six-membered chelate rings in *gauche* and *chair* conformations, respectively. In the complex anion, the  $\text{Ni}^{\text{II}}$  ion is coordinated by the two tridentate pdc<sup>2-</sup> ligands *via* their carboxylate and nitrogen atom donors in a distorted octahedral *trans*- $\text{NiO}_4\text{N}_2$  geometry with nearly orthogonal orientation of the planes defining the carboxylate rings and the average Ni–N bond length [1.965 (4) Å] shorter than the average Ni–O bond distance [2.113 (7) Å]. In the crystal, the NH donor groups of the tetraamine, the carboxylic groups of the pdc<sup>2-</sup> anion and the coordinated water molecules are involved in numerous N–H...O and O–H...O hydrogen bonds, leading to electroneutral sheets oriented parallel to the (001) plane.

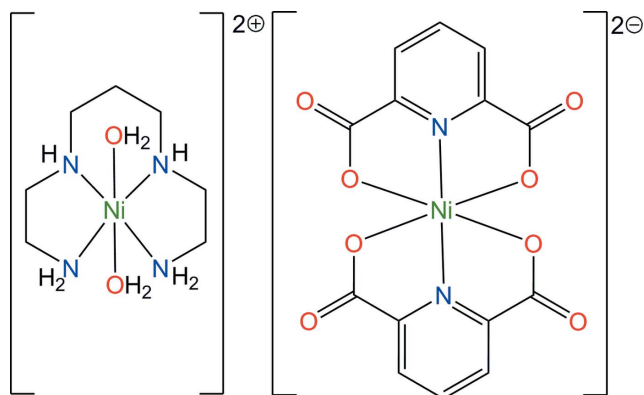
## 1. Chemical context

Crystalline coordination polymers possessing permanent porosity (metal–organic frameworks, MOFs) are of enormous current interest because of their potential for applications in different areas including gas storage, separation, catalysis, *etc.* (MacGillivray & Lukehart, 2014; Kaskel, 2016). Nickel(II) complexes of the 14-membered macrocyclic tetraamine ligands, in particular of cyclam and its C-alkylated derivatives (cyclam = 1,4,8,11-tetraazacyclotetradecane,  $\text{C}_{10}\text{H}_{24}\text{N}_4$ ), are widely used as metal-containing building units for the construction of MOFs (Lampeka & Tsymbal, 2004; Suh & Moon, 2007; Suh *et al.*, 2012; Stackhouse & Ma, 2018; Lee & Moon, 2018). At the same time, nickel(II) complexes of 1,4,8,11-tetraazaundecane ( $\text{C}_7\text{H}_{20}\text{N}_4$ ;  $L$ ) – the closest open-chain analogue of cyclam – are rarely utilized for the construction of MOFs and only a few examples of coordination polymers formed by the  $[\text{Ni}(L)]^{2+}$  cation with azide (Escuer *et al.*, 1993), cyanide (Koo *et al.*, 2003), and cyanometalate (Koo *et al.*, 2003; Shek *et al.*, 2005; Talukder *et al.*,



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2012; Ni *et al.*, 2014) bridging anions have been characterized by single-crystal X-ray diffraction.



Multidentate aromatic carboxylates are known as the most common linkers in MOFs (Rao *et al.*, 2004). Although the bridging properties of one of the simplest representative of this class of compounds, 1,3-benzenedicarboxylate, with macrocyclic nickel(II) cations are well studied (see, for example, Tsybmal *et al.*, 2021), coordination polymers based on its structural analogue, pyridine-2,6-dicarboxylate (C<sub>7</sub>H<sub>3</sub>NO<sub>4</sub><sup>2-</sup>; pdc<sup>2-</sup>), are confined to a sole example (Choi *et al.*, 2003). Interestingly, an attempt to prepare a coordination polymer containing the [Ni(cyclam)]<sup>2+</sup> cation with pdc<sup>2-</sup> led to the ionic product [Ni(cyclam)(H<sub>2</sub>O)<sub>2</sub>][Ni(pdc)<sub>2</sub>].2.5H<sub>2</sub>O due to sequestering of the metal ion from the cavity of the macrocycle by this chelating ligand (Park *et al.*, 2007).

As part of our research on MOFs formed by nickel(II) tetraaza cations and aromatic carboxylates, we report here the synthesis and crystal structure of the product of the reaction of [Ni(L)]<sup>2+</sup> with pdc<sup>2-</sup>, namely [*trans*-diaqua(1,4,8,11-tetraazaundecane-*k*<sup>4</sup>N<sup>1</sup>N<sup>4</sup>N<sup>8</sup>N<sup>11</sup>)nickel(II)][bis(pyridine-2,6-dicarboxylato-*κ*<sup>3</sup>N,O,O)nickel(II)], [Ni(L)(H<sub>2</sub>O)<sub>2</sub>][Ni(pdc)<sub>2</sub>], **I**. Similar to the reaction of pyridine-2,6-dicarboxylate with the

**Table 1**  
Selected geometric parameters (Å, °).

Ni1—O1	2.099 (2)	Ni2—O1W	2.131 (2)
Ni1—O3	2.109 (2)	Ni2—O2W	2.124 (2)
Ni1—O5	2.111 (2)	Ni2—N3	2.074 (2)
Ni1—O7	2.1343 (19)	Ni2—N4	2.088 (2)
Ni1—N1	1.961 (2)	Ni2—N5	2.095 (2)
Ni1—N2	1.969 (2)	Ni2—N6	2.089 (3)
O1—Ni1—O3	156.79 (8)	O2W—Ni2—O1W	174.88 (8)
O1—Ni1—O5	95.74 (8)	N3—Ni2—O1W	86.26 (9)
O1—Ni1—O7	89.96 (8)	N3—Ni2—O2W	92.25 (9)
O3—Ni1—O5	89.36 (8)	N3—Ni2—N4	84.10 (10)
O3—Ni1—O7	94.68 (8)	N3—Ni2—N5	174.54 (10)
O5—Ni1—O7	155.62 (7)	N3—Ni2—N6	101.01 (10)
N1—Ni1—O1	78.63 (9)	N4—Ni2—O1W	87.83 (9)
N1—Ni1—O3	78.19 (9)	N4—Ni2—O2W	96.90 (9)
N1—Ni1—O5	105.53 (9)	N4—Ni2—N5	90.45 (10)
N1—Ni1—O7	98.84 (9)	N4—Ni2—N6	172.57 (10)
N1—Ni1—N2	176.06 (10)	N5—Ni2—O1W	93.07 (9)
N2—Ni1—O1	99.61 (9)	N5—Ni2—O2W	88.86 (9)
N2—Ni1—O3	103.60 (9)	N6—Ni2—O1W	87.13 (9)
N2—Ni1—O5	78.10 (9)	N6—Ni2—O2W	88.34 (9)
N2—Ni1—O7	77.58 (9)	N6—Ni2—N5	84.36 (10)

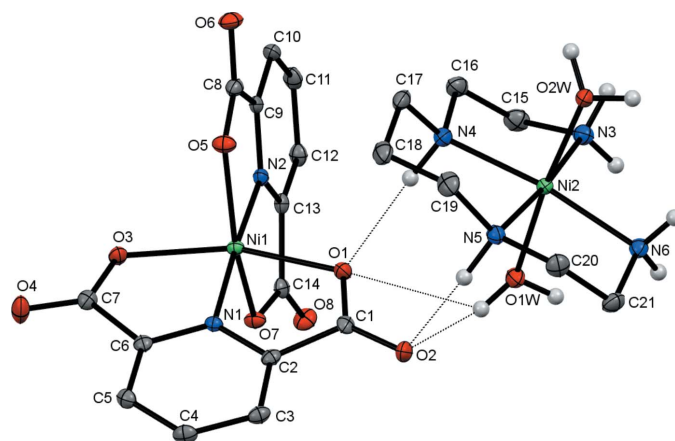
[Ni(cyclam)]<sup>2+</sup> cation, the formation of the title compound is explained by the sequestering of the metal ion from the starting cation with the formation of the [Ni(pdc)<sub>2</sub>]<sup>2-</sup> anion. Additionally, to the best of our knowledge, the structure of the [*trans*-diaqua(1,4,8,11-tetraazaundecane)nickel(II)] moiety has not previously been reported in the literature.

## 2. Structural commentary

The molecular structure of the title compound **I** is shown in Fig. 1. Atom Ni1 is coordinated by the two tridentate pdc<sup>2-</sup> ligands *via* their carboxylate and nitrogen donors, resulting in the formation of the [Ni(pdc)<sub>2</sub>]<sup>2-</sup> divalent anion, which is charge-balanced by the [Ni(L)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> divalent cation formed by atom Ni2.

The coordination polyhedron of Ni1<sup>II</sup> in the complex anion ion can be described as a tetragonally compressed *trans*-NiO<sub>4</sub>N<sub>2</sub> octahedron with the Ni—N bond lengths [average value 1.965 (4) Å] shorter than the Ni—O ones [average value 2.113 (7) Å] (Table 1). Another source of distortion is the alternating displacement (by *ca* 0.43 Å) of the coordinated oxygen atoms of deprotonated carboxylic groups from the mean equatorial plane formed by the four oxygen atoms. The values of the bite angles in the five-membered chelate rings in the complex anion are very similar (Table 1). The pdc<sup>2-</sup> carboxylate rings are oriented nearly orthogonally with an angle of 81.5 (3)° between their mean planes.

The Ni2<sup>II</sup> ion in the complex cation is coordinated by the four N atoms of the ligand *L* and the mutually *trans* O atoms of the water molecules in a tetragonally elongated *trans*-NiN<sub>4</sub>O<sub>2</sub> octahedral geometry with the average equatorial Ni—N bond length slightly shorter than the average axial Ni—O bond [2.087 (4) and 2.128 (4) Å, respectively (Table 1)]. The ligand *L* in **I** adopts its energetically favored conformation with the five-membered and six-membered chelate rings in *gauche* and *chair* conformations, respectively, which resemble



**Figure 1**  
View of the molecular structure of **I**, showing the partial atom-labeling scheme, with displacement ellipsoids drawn at the 40% probability level. C-bound H atoms are omitted for clarity. Hydrogen-bonding interactions are shown as dotted lines.

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

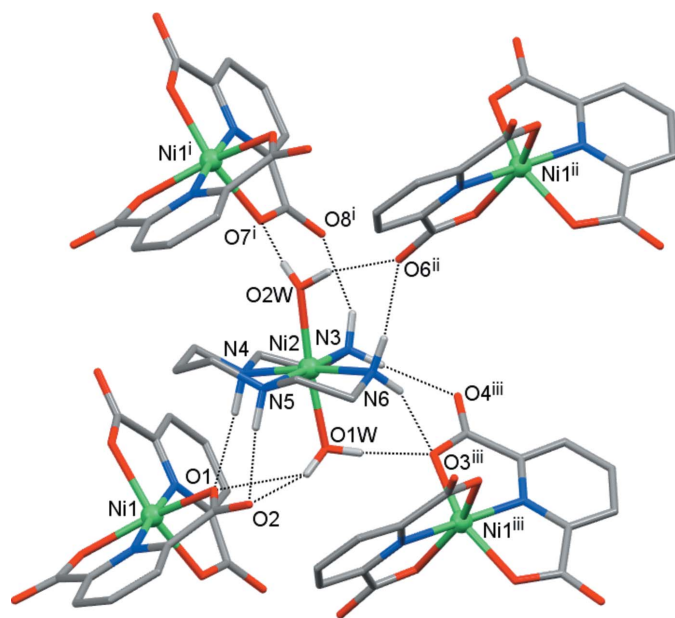
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N3-H3A\cdots O8^i$	0.91	2.41	3.213 (3)	147
$N3-H3B\cdots O4^{ii}$	0.91	2.11	3.015 (3)	176
$N4-H4A\cdots O1$	1.00	2.07	3.054 (3)	167
$N5-H5A\cdots O2$	1.00	2.08	3.054 (3)	163
$N6-H6A\cdots O3^{ii}$	0.91	2.14	2.986 (3)	154
$N6-H6B\cdots O6^{iii}$	0.91	2.07	2.943 (3)	160
$O1W-H1WA\cdots O1$	0.86	2.56	3.088 (3)	121
$O1W-H1WA\cdots O2$	0.86	2.00	2.795 (3)	154
$O1W-H1WB\cdots O3^{ii}$	0.86	1.91	2.757 (3)	170
$O2W-H2WA\cdots O7^i$	0.87	1.80	2.663 (3)	169
$O2W-H2WB\cdots O6^{iii}$	0.87	1.90	2.742 (3)	160

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

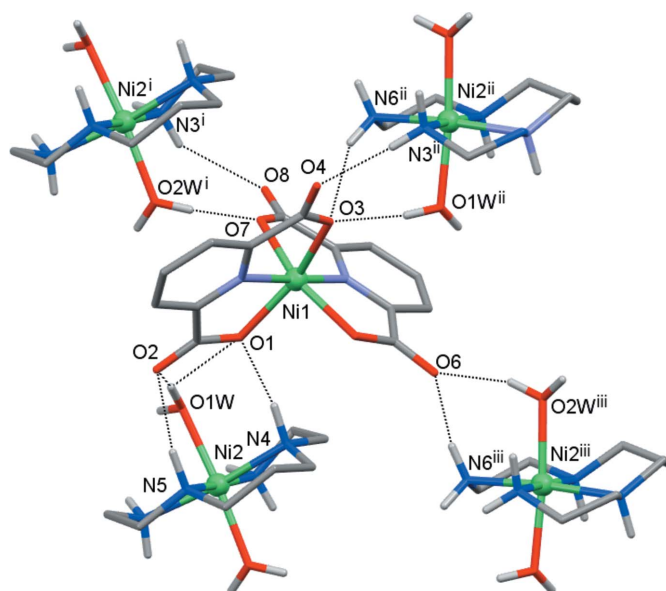
the *trans*-III configuration usually observed in cyclam complexes (Bosnich *et al.*, 1965). This conformation is also characteristic of the macrocyclic ligand in  $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$  (Park *et al.*, 2007), although the bite angles in the five-membered ( $85.54^\circ$ ) and six-membered ( $94.46^\circ$ ) chelate rings are correspondingly larger and smaller compared to those in **I** (Table 1).

### 3. Supramolecular features

The crystals of **I** are composed of  $[\text{Ni}(L)(\text{H}_2\text{O})_2]^{2+}$  complex cations and  $[\text{Ni}(\text{pdc})_2]^{2-}$  anions connected by numerous hydrogen bonds (Table 2). Each ion is surrounded by four counter-ions (Figs. 2 and 3); the cation acts as the hydrogen-bond donor due to the presence of the N–H fragments of

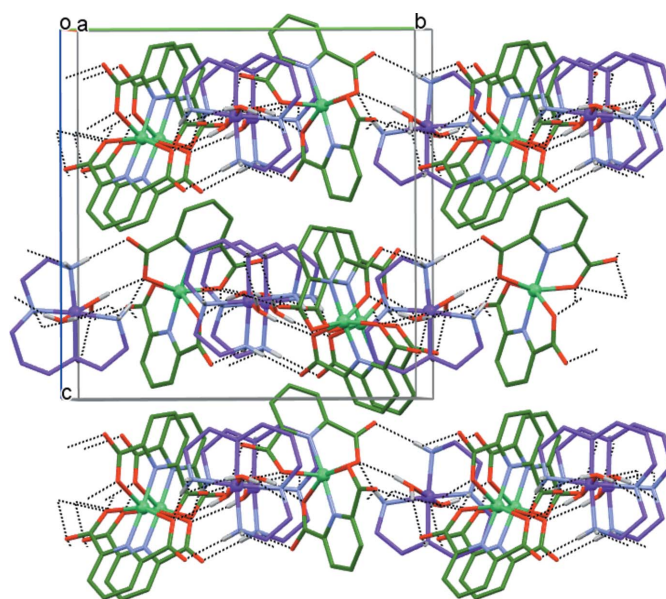


**Figure 2**  
 Nearest surroundings of the cation in **I** formed by hydrogen bonding (dotted lines). [Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$ .]



**Figure 3**  
 Nearest surroundings of the anion in **I** formed by hydrogen bonding (dotted lines). [Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ .]

amino groups and the O–H groups of coordinated water molecules, while the anion displays proton-acceptor properties because of the availability of the carboxylic groups. These aggregates are further arranged into two-dimensional sheets oriented parallel to the (001) plane (Fig. 4). There are no hydrogen-bonding contacts between the sheets, and the three-



**Figure 4**  
 Electroneutral sheets of the complex ions in **I** parallel to the (001) plane. C-bound H atoms are omitted for clarity. C atoms of the cation and anion are shown in purple and green, respectively. Hydrogen bonds are shown as dotted lines.

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	[Ni(C <sub>7</sub> H <sub>20</sub> N <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> ] [Ni(C <sub>7</sub> H <sub>3</sub> NO <sub>4</sub> ) <sub>2</sub> ]
<i>M<sub>r</sub></i>	643.93
Crystal system, space group	Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.3219 (6), 16.3211 (10), 16.9483 (8)
<i>V</i> (Å <sup>3</sup> )	2578.6 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm <sup>-1</sup> )	1.53
Crystal size (mm)	0.25 × 0.2 × 0.2
Data collection	
Diffraction	Broker APEXII CCD
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2019)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.705, 0.737
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	36128, 4909, 4668
<i>R<sub>int</sub></i>	0.045
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.610
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> [ <i>F</i> <sup>2</sup> ], <i>S</i>	0.021, 0.050, 1.04
No. of reflections	4909
No. of parameters	356
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.49, -0.26
Absolute structure	Flack <i>x</i> determined using 1953 quotients [( <i>I</i> <sup>+</sup> ) - ( <i>I</i> <sup>-</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	-0.010 (4)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

dimensional coherence of the crystal is provided by van der Waals interactions.

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.42, last update February 2021; Groom *et al.*, 2016) indicated that no compounds containing the [Ni(*L*)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> cation have been structurally characterized to date, the closest analogue being the complex [Ni(*L*)(H<sub>2</sub>O)(Cl)]Cl (refcode UMOFEH; Oblezov *et al.*, 2003). In general, the geometrical parameters of both cations in these compounds are similar, although the Ni–O bond length in the latter is longer (2.182 Å), probably because of the *trans* influence of the chloride ligand.

As far as the structures of the cations in the compounds with the same bis(pyridine-2,6-dicarboxylato)-nickel(II) anion are concerned, {[Ni(*L*)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> in **I** and [Ni(cyclam)-(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> in TICJEV (Park *et al.*, 2007)}, a higher tetragonal distortion of the coordination polyhedron in the latter case [average Ni–N bond length of 2.068 (6) Å and Ni–O bond length of 2.152 Å] should be mentioned, which can be explained by the stronger *cis* influence of the macrocyclic

ligand compared to the non-cyclic one (Yatsimirskii & Lampeka, 1985).

#### 5. Synthesis and crystallization

All chemicals and solvents used in this work were purchased from Sigma–Aldrich and used without further purification. The complex [Ni(*L*)](ClO<sub>4</sub>)<sub>2</sub> was prepared by mixing equimolar amount of *L* and nickel perchlorate hexahydrate in ethanol. The title compound **I** was prepared as follows. A solution of [Ni(*L*)](ClO<sub>4</sub>)<sub>2</sub> (11 mg, 0.026 mmol) in 1 ml of DMF was added to 0.4 ml of an aqueous solution of Na<sub>2</sub>(pdc) (2.7 mg, 0.013 mmol). Blue crystals formed in a day, which were filtered off, washed with diethyl ether and dried in air. Yield: 1.3 mg (15.5%). Analysis calculated for C<sub>21</sub>H<sub>30</sub>N<sub>6</sub>Ni<sub>2</sub>O<sub>10</sub>: C 39.17, H 4.66, N 13.06%. Found: C 39.04, H 5.0, N 13.21%. Single crystals of **I** suitable for X-ray diffraction analysis were selected from the sample resulting from the synthesis.

**Safety note:** Perchlorate salts of metal complexes are potentially explosive and should be handled with care.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms in **I** were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances of 0.95 (ring H atoms) or 0.99 Å (aliphatic H atoms), N–H distances of 0.91 (primary amino groups) or 1.00 Å (secondary aminogroups) with *U*<sub>iso</sub>(H) values of 1.2*U*<sub>eq</sub> of the parent atoms. Water H atoms were positioned geometrically (O–H = 0.71–0.85 Å) and refined as riding with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O).

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## supporting information

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## Crystal structure of *trans*-diaqua(1,4,8,11-tetraazaundecane)nickel(II) bis-(pyridine-2,6-dicarboxylato)nickel(II)

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### Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2019); cell refinement: *CrysAlis PRO* (Rigaku OD, 2019); data reduction: *CrysAlis PRO* (Rigaku OD, 2019); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

*trans*-Diaqua(1,4,8,11-tetraazaundecane- $\kappa^4N^1,N^4,N^8,N^{11}$ )nickel(II) bis(pyridine-2,6-dicarboxylato- $\kappa^3O^2,N,O^6$ )nickel(II)

### Crystal data

[Ni(C<sub>7</sub>H<sub>20</sub>N<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>][Ni(C<sub>7</sub>H<sub>5</sub>NO<sub>4</sub>)<sub>2</sub>]

$M_r = 643.93$

Orthorhombic,  $P2_12_12_1$

$a = 9.3219$  (6) Å

$b = 16.3211$  (10) Å

$c = 16.9483$  (8) Å

$V = 2578.6$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 1336$

$D_x = 1.659$  Mg m<sup>-3</sup>

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

Cell parameters from 8341 reflections

$\theta = 2.5$ – $25.3^\circ$

$\mu = 1.53$  mm<sup>-1</sup>

$T = 100$  K

Prism, clear light pink

$0.25 \times 0.2 \times 0.2$  mm

### Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*CrysAlisPro*; Rigaku OD, 2019)

$T_{\min} = 0.705$ ,  $T_{\max} = 0.737$

36128 measured reflections

4909 independent reflections

4668 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 25.7^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -11 \rightarrow 11$

$k = -19 \rightarrow 19$

$l = -20 \rightarrow 20$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.050$

$S = 1.04$

4909 reflections

356 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 0.7375P]$

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

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.49$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.26$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using  
1953 quotients  $[(F^+)-(F^-)]/[(F^+)+(F^-)]$  (Parsons *et al.*, 2013)  
Absolute structure parameter:  $-0.010$  (4)

### Special details

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

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

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	1.09379 (4)	0.79146 (2)	0.79300 (2)	0.01132 (9)
O1	0.9734 (2)	0.89973 (12)	0.80207 (12)	0.0156 (4)
O3	1.2374 (2)	0.69917 (13)	0.82970 (11)	0.0150 (4)
O2	0.9525 (2)	1.01235 (13)	0.87640 (12)	0.0190 (5)
O4	1.3661 (3)	0.65997 (13)	0.93534 (13)	0.0250 (5)
O5	0.9208 (2)	0.71131 (13)	0.81555 (11)	0.0178 (4)
O7	1.2475 (2)	0.85377 (12)	0.72153 (10)	0.0151 (4)
O6	0.7669 (2)	0.62760 (13)	0.75366 (12)	0.0208 (5)
O8	1.2894 (2)	0.88805 (13)	0.59530 (12)	0.0197 (5)
N1	1.1543 (3)	0.83219 (15)	0.89664 (13)	0.0117 (5)
N2	1.0390 (3)	0.75735 (15)	0.68573 (13)	0.0124 (5)
C1	1.0034 (3)	0.94313 (19)	0.86156 (17)	0.0147 (6)
C2	1.1083 (3)	0.90574 (17)	0.91977 (15)	0.0136 (6)
C3	1.1561 (3)	0.93967 (19)	0.98988 (17)	0.0160 (6)
H3	1.127255	0.993102	1.005442	0.019*
C4	1.2481 (3)	0.89317 (19)	1.03707 (17)	0.0178 (7)
H4	1.278944	0.913881	1.086623	0.021*
C5	1.2944 (3)	0.81687 (19)	1.01178 (16)	0.0155 (6)
H5	1.357733	0.785035	1.043217	0.019*
C6	1.2463 (3)	0.78819 (18)	0.93978 (16)	0.0136 (6)
C7	1.2889 (3)	0.70808 (19)	0.90009 (17)	0.0154 (6)
C8	0.8683 (3)	0.67716 (17)	0.75527 (17)	0.0149 (6)
C9	0.9355 (3)	0.70262 (18)	0.67704 (17)	0.0131 (6)
C10	0.8957 (4)	0.67512 (17)	0.60250 (17)	0.0166 (6)
H10	0.821798	0.635587	0.596314	0.020*
C11	0.9667 (3)	0.7068 (2)	0.53760 (18)	0.0194 (7)
H11	0.941943	0.688728	0.486084	0.023*
C12	1.0745 (3)	0.76525 (18)	0.54766 (16)	0.0164 (6)
H12	1.123225	0.787779	0.503466	0.020*
C13	1.1087 (3)	0.78960 (17)	0.62377 (16)	0.0132 (6)
C14	1.2247 (3)	0.84969 (18)	0.64704 (16)	0.0147 (6)
Ni2	0.58765 (4)	1.01066 (2)	0.76468 (2)	0.01201 (9)
O1W	0.8016 (2)	1.04716 (13)	0.73792 (12)	0.0192 (5)
H1WA	0.869828	1.041746	0.771368	0.031 (10)*
H1WB	0.797698	1.092906	0.712918	0.040 (11)*

O2W	0.3684 (2)	0.98471 (13)	0.78767 (12)	0.0172 (4)
H2WA	0.325706	0.939783	0.772223	0.042 (12)*
H2WB	0.308376	1.025333	0.781113	0.069 (16)*
N3	0.5586 (3)	1.00016 (16)	0.64375 (14)	0.0192 (6)
H3A	0.465077	0.989548	0.632344	0.023*
H3B	0.584859	1.047317	0.618999	0.023*
N4	0.6569 (3)	0.88925 (15)	0.75663 (15)	0.0174 (5)
H4A	0.763467	0.890194	0.763131	0.021*
N5	0.6255 (3)	1.01005 (15)	0.88651 (13)	0.0163 (5)
H5A	0.731507	1.013124	0.894920	0.020*
N6	0.5419 (3)	1.13467 (15)	0.78184 (14)	0.0170 (6)
H6A	0.586732	1.165700	0.744666	0.020*
H6B	0.445736	1.143679	0.778488	0.020*
C15	0.6505 (4)	0.9317 (2)	0.61828 (18)	0.0236 (7)
H15A	0.752369	0.948818	0.618268	0.028*
H15B	0.624339	0.914509	0.564135	0.028*
C16	0.6286 (4)	0.8613 (2)	0.67532 (19)	0.0226 (8)
H16A	0.528893	0.840840	0.671222	0.027*
H16B	0.694390	0.815805	0.661796	0.027*
C17	0.6005 (4)	0.83218 (18)	0.81722 (18)	0.0210 (7)
H17A	0.639786	0.776760	0.807346	0.025*
H17B	0.494866	0.829025	0.812244	0.025*
C18	0.6383 (4)	0.8580 (2)	0.90014 (19)	0.0234 (8)
H18A	0.743906	0.863351	0.903632	0.028*
H18B	0.609403	0.813510	0.936547	0.028*
C19	0.5716 (4)	0.93725 (19)	0.92903 (18)	0.0230 (7)
H19A	0.466236	0.934035	0.922537	0.028*
H19B	0.592126	0.943637	0.986010	0.028*
C20	0.5617 (4)	1.0860 (2)	0.91737 (18)	0.0216 (8)
H20A	0.601711	1.098266	0.970176	0.026*
H20B	0.456571	1.079348	0.922625	0.026*
C21	0.5947 (4)	1.15564 (18)	0.86117 (17)	0.0207 (7)
H21A	0.547856	1.206507	0.879817	0.025*
H21B	0.699559	1.165229	0.859354	0.025*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.01194 (18)	0.01160 (18)	0.01043 (16)	-0.00100 (17)	-0.00079 (17)	-0.00127 (13)
O1	0.0139 (10)	0.0152 (11)	0.0177 (10)	0.0013 (9)	-0.0033 (8)	-0.0023 (9)
O3	0.0179 (11)	0.0130 (11)	0.0142 (10)	0.0014 (9)	-0.0025 (9)	-0.0030 (8)
O2	0.0168 (11)	0.0133 (11)	0.0270 (11)	0.0034 (9)	-0.0032 (8)	-0.0013 (9)
O4	0.0324 (14)	0.0204 (13)	0.0222 (11)	0.0110 (10)	-0.0066 (10)	-0.0003 (9)
O5	0.0170 (11)	0.0199 (11)	0.0164 (10)	-0.0050 (11)	0.0015 (9)	-0.0006 (8)
O7	0.0161 (11)	0.0165 (11)	0.0126 (11)	-0.0039 (9)	-0.0008 (8)	-0.0009 (8)
O6	0.0182 (12)	0.0174 (11)	0.0267 (12)	-0.0069 (10)	0.0006 (9)	-0.0020 (9)
O8	0.0209 (12)	0.0198 (12)	0.0185 (11)	-0.0028 (10)	0.0058 (9)	0.0036 (9)
N1	0.0110 (12)	0.0126 (13)	0.0115 (12)	-0.0015 (10)	0.0003 (10)	-0.0001 (10)



N2	0.0113 (12)	0.0116 (13)	0.0141 (12)	0.0025 (10)	-0.0014 (9)	-0.0013 (10)
C1	0.0084 (16)	0.0155 (17)	0.0203 (15)	0.0004 (13)	0.0032 (12)	0.0010 (12)
C2	0.0135 (16)	0.0124 (15)	0.0148 (13)	-0.0028 (13)	0.0030 (12)	0.0004 (11)
C3	0.0179 (16)	0.0148 (17)	0.0153 (14)	-0.0031 (13)	0.0037 (12)	-0.0031 (12)
C4	0.0216 (18)	0.0201 (17)	0.0117 (13)	-0.0037 (14)	0.0006 (12)	-0.0027 (12)
C5	0.0159 (16)	0.0180 (17)	0.0127 (14)	-0.0021 (13)	-0.0009 (12)	0.0028 (12)
C6	0.0123 (15)	0.0138 (15)	0.0148 (14)	-0.0024 (13)	0.0020 (11)	0.0025 (11)
C7	0.0150 (15)	0.0151 (16)	0.0160 (14)	0.0002 (13)	0.0029 (12)	0.0002 (12)
C8	0.0126 (16)	0.0118 (15)	0.0204 (16)	0.0002 (12)	0.0017 (12)	0.0001 (12)
C9	0.0103 (15)	0.0100 (14)	0.0190 (14)	0.0026 (12)	-0.0021 (11)	-0.0010 (11)
C10	0.0160 (16)	0.0127 (15)	0.0212 (15)	0.0007 (14)	-0.0074 (14)	-0.0018 (11)
C11	0.0226 (17)	0.0200 (17)	0.0154 (14)	0.0049 (14)	-0.0060 (12)	-0.0026 (13)
C12	0.0194 (17)	0.0177 (16)	0.0122 (13)	0.0032 (14)	-0.0009 (12)	0.0019 (11)
C13	0.0132 (15)	0.0121 (14)	0.0142 (13)	0.0041 (13)	0.0001 (12)	0.0012 (11)
C14	0.0110 (15)	0.0142 (16)	0.0191 (15)	0.0044 (13)	0.0012 (12)	-0.0013 (12)
Ni2	0.01145 (18)	0.01053 (18)	0.01407 (17)	-0.00027 (16)	-0.00135 (15)	0.00039 (13)
O1W	0.0169 (12)	0.0177 (12)	0.0231 (11)	-0.0015 (9)	-0.0018 (9)	0.0056 (9)
O2W	0.0143 (10)	0.0127 (11)	0.0247 (11)	0.0001 (9)	-0.0021 (8)	0.0009 (9)
N3	0.0191 (15)	0.0190 (15)	0.0195 (13)	-0.0019 (12)	-0.0024 (10)	0.0010 (11)
N4	0.0147 (13)	0.0142 (14)	0.0232 (13)	0.0001 (11)	-0.0017 (10)	-0.0007 (11)
N5	0.0148 (14)	0.0166 (13)	0.0174 (12)	-0.0005 (11)	-0.0015 (10)	0.0031 (10)
N6	0.0156 (13)	0.0147 (13)	0.0207 (14)	0.0001 (10)	0.0007 (10)	0.0028 (11)
C15	0.0248 (18)	0.0260 (19)	0.0201 (16)	0.0000 (15)	-0.0007 (13)	-0.0062 (14)
C16	0.0199 (19)	0.0188 (18)	0.0292 (17)	0.0016 (14)	-0.0029 (13)	-0.0074 (14)
C17	0.0163 (16)	0.0118 (15)	0.0350 (17)	0.0008 (14)	0.0018 (15)	0.0018 (12)
C18	0.0204 (18)	0.0197 (18)	0.0301 (18)	-0.0005 (14)	0.0004 (14)	0.0097 (14)
C19	0.0228 (19)	0.0250 (19)	0.0213 (15)	-0.0020 (15)	0.0025 (14)	0.0091 (13)
C20	0.025 (2)	0.0221 (18)	0.0179 (15)	0.0019 (14)	0.0001 (13)	-0.0043 (13)
C21	0.0234 (17)	0.0136 (15)	0.0252 (16)	-0.0018 (16)	0.0012 (16)	-0.0046 (12)

*Geometric parameters (Å, °)*

Ni1—O1	2.099 (2)	Ni2—N3	2.074 (2)
Ni1—O3	2.109 (2)	Ni2—N4	2.088 (2)
Ni1—O5	2.111 (2)	Ni2—N5	2.095 (2)
Ni1—O7	2.1343 (19)	Ni2—N6	2.089 (3)
Ni1—N1	1.961 (2)	O1W—H1WA	0.8563
Ni1—N2	1.969 (2)	O1W—H1WB	0.8593
O1—C1	1.264 (4)	O2W—H2WA	0.8743
O3—C7	1.294 (3)	O2W—H2WB	0.8744
O2—C1	1.251 (4)	N3—H3A	0.9100
O4—C7	1.221 (4)	N3—H3B	0.9100
O5—C8	1.262 (3)	N3—C15	1.473 (4)
O7—C14	1.282 (3)	N4—H4A	1.0000
O6—C8	1.245 (3)	N4—C16	1.475 (4)
O8—C14	1.235 (4)	N4—C17	1.483 (4)
N1—C2	1.334 (4)	N5—H5A	1.0000
N1—C6	1.336 (4)	N5—C19	1.477 (4)

N2—C9	1.323 (4)	N5—C20	1.471 (4)
N2—C13	1.343 (4)	N6—H6A	0.9100
C1—C2	1.517 (4)	N6—H6B	0.9100
C2—C3	1.385 (4)	N6—C21	1.472 (4)
C3—H3	0.9500	C15—H15A	0.9900
C3—C4	1.396 (4)	C15—H15B	0.9900
C4—H4	0.9500	C15—C16	1.515 (5)
C4—C5	1.386 (4)	C16—H16A	0.9900
C5—H5	0.9500	C16—H16B	0.9900
C5—C6	1.382 (4)	C17—H17A	0.9900
C6—C7	1.523 (4)	C17—H17B	0.9900
C8—C9	1.524 (4)	C17—C18	1.509 (4)
C9—C10	1.391 (4)	C18—H18A	0.9900
C10—H10	0.9500	C18—H18B	0.9900
C10—C11	1.384 (4)	C18—C19	1.517 (5)
C11—H11	0.9500	C19—H19A	0.9900
C11—C12	1.396 (5)	C19—H19B	0.9900
C12—H12	0.9500	C20—H20A	0.9900
C12—C13	1.387 (4)	C20—H20B	0.9900
C13—C14	1.512 (4)	C20—C21	1.515 (4)
Ni2—O1W	2.131 (2)	C21—H21A	0.9900
Ni2—O2W	2.124 (2)	C21—H21B	0.9900
O1—Ni1—O3	156.79 (8)	N5—Ni2—O1W	93.07 (9)
O1—Ni1—O5	95.74 (8)	N5—Ni2—O2W	88.86 (9)
O1—Ni1—O7	89.96 (8)	N6—Ni2—O1W	87.13 (9)
O3—Ni1—O5	89.36 (8)	N6—Ni2—O2W	88.34 (9)
O3—Ni1—O7	94.68 (8)	N6—Ni2—N5	84.36 (10)
O5—Ni1—O7	155.62 (7)	Ni2—O1W—H1WA	121.7
N1—Ni1—O1	78.63 (9)	Ni2—O1W—H1WB	107.9
N1—Ni1—O3	78.19 (9)	H1WA—O1W—H1WB	116.6
N1—Ni1—O5	105.53 (9)	Ni2—O2W—H2WA	123.4
N1—Ni1—O7	98.84 (9)	Ni2—O2W—H2WB	116.2
N1—Ni1—N2	176.06 (10)	H2WA—O2W—H2WB	107.9
N2—Ni1—O1	99.61 (9)	Ni2—N3—H3A	110.5
N2—Ni1—O3	103.60 (9)	Ni2—N3—H3B	110.5
N2—Ni1—O5	78.10 (9)	H3A—N3—H3B	108.7
N2—Ni1—O7	77.58 (9)	C15—N3—Ni2	106.06 (18)
C1—O1—Ni1	114.33 (19)	C15—N3—H3A	110.5
C7—O3—Ni1	115.29 (18)	C15—N3—H3B	110.5
C8—O5—Ni1	115.02 (18)	Ni2—N4—H4A	106.6
C14—O7—Ni1	115.00 (19)	C16—N4—Ni2	107.41 (19)
C2—N1—Ni1	118.40 (19)	C16—N4—H4A	106.6
C2—N1—C6	122.0 (3)	C16—N4—C17	112.9 (2)
C6—N1—Ni1	119.5 (2)	C17—N4—Ni2	116.20 (19)
C9—N2—Ni1	118.88 (19)	C17—N4—H4A	106.6
C9—N2—C13	122.1 (2)	Ni2—N5—H5A	107.9
C13—N2—Ni1	119.07 (19)	C19—N5—Ni2	115.30 (19)

O1—C1—C2	115.9 (3)	C19—N5—H5A	107.9
O2—C1—O1	125.6 (3)	C20—N5—Ni2	106.17 (18)
O2—C1—C2	118.5 (3)	C20—N5—H5A	107.9
N1—C2—C1	112.2 (2)	C20—N5—C19	111.5 (2)
N1—C2—C3	120.6 (3)	Ni2—N6—H6A	110.4
C3—C2—C1	127.2 (3)	Ni2—N6—H6B	110.4
C2—C3—H3	120.9	H6A—N6—H6B	108.6
C2—C3—C4	118.1 (3)	C21—N6—Ni2	106.50 (18)
C4—C3—H3	120.9	C21—N6—H6A	110.4
C3—C4—H4	119.9	C21—N6—H6B	110.4
C5—C4—C3	120.2 (3)	N3—C15—H15A	110.1
C5—C4—H4	119.9	N3—C15—H15B	110.1
C4—C5—H5	120.8	N3—C15—C16	108.1 (3)
C6—C5—C4	118.4 (3)	H15A—C15—H15B	108.4
C6—C5—H5	120.8	C16—C15—H15A	110.1
N1—C6—C5	120.6 (3)	C16—C15—H15B	110.1
N1—C6—C7	112.8 (2)	N4—C16—C15	109.7 (3)
C5—C6—C7	126.6 (3)	N4—C16—H16A	109.7
O3—C7—C6	114.0 (3)	N4—C16—H16B	109.7
O4—C7—O3	126.7 (3)	C15—C16—H16A	109.7
O4—C7—C6	119.3 (3)	C15—C16—H16B	109.7
O5—C8—C9	115.1 (2)	H16A—C16—H16B	108.2
O6—C8—O5	126.8 (3)	N4—C17—H17A	109.0
O6—C8—C9	118.0 (3)	N4—C17—H17B	109.0
N2—C9—C8	112.7 (2)	N4—C17—C18	112.8 (3)
N2—C9—C10	120.9 (3)	H17A—C17—H17B	107.8
C10—C9—C8	126.4 (3)	C18—C17—H17A	109.0
C9—C10—H10	120.8	C18—C17—H17B	109.0
C11—C10—C9	118.3 (3)	C17—C18—H18A	108.2
C11—C10—H10	120.8	C17—C18—H18B	108.2
C10—C11—H11	119.9	C17—C18—C19	116.3 (3)
C10—C11—C12	120.1 (3)	H18A—C18—H18B	107.4
C12—C11—H11	119.9	C19—C18—H18A	108.2
C11—C12—H12	120.8	C19—C18—H18B	108.2
C13—C12—C11	118.4 (3)	N5—C19—C18	112.9 (3)
C13—C12—H12	120.8	N5—C19—H19A	109.0
N2—C13—C12	120.2 (3)	N5—C19—H19B	109.0
N2—C13—C14	113.4 (2)	C18—C19—H19A	109.0
C12—C13—C14	126.4 (3)	C18—C19—H19B	109.0
O7—C14—C13	114.2 (3)	H19A—C19—H19B	107.8
O8—C14—O7	126.3 (3)	N5—C20—H20A	109.9
O8—C14—C13	119.5 (3)	N5—C20—H20B	109.9
O2W—Ni2—O1W	174.88 (8)	N5—C20—C21	109.1 (2)
N3—Ni2—O1W	86.26 (9)	H20A—C20—H20B	108.3
N3—Ni2—O2W	92.25 (9)	C21—C20—H20A	109.9
N3—Ni2—N4	84.10 (10)	C21—C20—H20B	109.9
N3—Ni2—N5	174.54 (10)	N6—C21—C20	109.4 (2)
N3—Ni2—N6	101.01 (10)	N6—C21—H21A	109.8

N4—Ni2—O1W	87.83 (9)	N6—C21—H21B	109.8
N4—Ni2—O2W	96.90 (9)	C20—C21—H21A	109.8
N4—Ni2—N5	90.45 (10)	C20—C21—H21B	109.8
N4—Ni2—N6	172.57 (10)	H21A—C21—H21B	108.2
Ni1—O1—C1—O2	175.1 (2)	C2—C3—C4—C5	3.0 (4)
Ni1—O1—C1—C2	-6.2 (3)	C3—C4—C5—C6	-0.7 (4)
Ni1—O3—C7—O4	175.0 (3)	C4—C5—C6—N1	-1.7 (4)
Ni1—O3—C7—C6	-5.5 (3)	C4—C5—C6—C7	177.3 (3)
Ni1—O5—C8—O6	179.7 (2)	C5—C6—C7—O3	-174.5 (3)
Ni1—O5—C8—C9	-2.3 (3)	C5—C6—C7—O4	5.0 (5)
Ni1—O7—C14—O8	171.5 (2)	C6—N1—C2—C1	-179.3 (2)
Ni1—O7—C14—C13	-10.1 (3)	C6—N1—C2—C3	0.7 (4)
Ni1—N1—C2—C1	4.6 (3)	C8—C9—C10—C11	178.3 (3)
Ni1—N1—C2—C3	-175.4 (2)	C9—N2—C13—C12	-0.7 (4)
Ni1—N1—C6—C5	177.8 (2)	C9—N2—C13—C14	-178.9 (3)
Ni1—N1—C6—C7	-1.4 (3)	C9—C10—C11—C12	-0.4 (4)
Ni1—N2—C9—C8	2.9 (3)	C10—C11—C12—C13	0.6 (5)
Ni1—N2—C9—C10	-178.3 (2)	C11—C12—C13—N2	-0.1 (4)
Ni1—N2—C13—C12	178.5 (2)	C11—C12—C13—C14	177.9 (3)
Ni1—N2—C13—C14	0.3 (3)	C12—C13—C14—O7	-171.3 (3)
O1—C1—C2—N1	1.4 (4)	C12—C13—C14—O8	7.2 (5)
O1—C1—C2—C3	-178.6 (3)	C13—N2—C9—C8	-177.9 (2)
O2—C1—C2—N1	-179.8 (3)	C13—N2—C9—C10	1.0 (4)
O2—C1—C2—C3	0.2 (5)	Ni2—N3—C15—C16	45.9 (3)
O5—C8—C9—N2	-0.2 (4)	Ni2—N4—C16—C15	34.9 (3)
O5—C8—C9—C10	-178.9 (3)	Ni2—N4—C17—C18	-59.1 (3)
O6—C8—C9—N2	178.0 (3)	Ni2—N5—C19—C18	60.4 (3)
O6—C8—C9—C10	-0.8 (4)	Ni2—N5—C20—C21	-41.5 (3)
N1—C2—C3—C4	-3.0 (4)	Ni2—N6—C21—C20	-40.1 (3)
N1—C6—C7—O3	4.6 (4)	N3—C15—C16—N4	-55.3 (3)
N1—C6—C7—O4	-175.8 (3)	N4—C17—C18—C19	65.8 (4)
N2—C9—C10—C11	-0.4 (4)	N5—C20—C21—N6	56.4 (3)
N2—C13—C14—O7	6.8 (4)	C16—N4—C17—C18	176.1 (3)
N2—C13—C14—O8	-174.7 (3)	C17—N4—C16—C15	164.3 (3)
C1—C2—C3—C4	177.0 (3)	C17—C18—C19—N5	-67.0 (4)
C2—N1—C6—C5	1.8 (4)	C19—N5—C20—C21	-167.8 (3)
C2—N1—C6—C7	-177.4 (3)	C20—N5—C19—C18	-178.4 (3)

## Hydrogen-bond geometry (Å, °)

<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>
N3—H3A $\cdots$ O8 <sup>i</sup>	0.91	2.41	3.213 (3)	147
N3—H3B $\cdots$ O4 <sup>ii</sup>	0.91	2.11	3.015 (3)	176
N4—H4A $\cdots$ O1	1.00	2.07	3.054 (3)	167
N5—H5A $\cdots$ O2	1.00	2.08	3.054 (3)	163
N6—H6A $\cdots$ O3 <sup>ii</sup>	0.91	2.14	2.986 (3)	154
N6—H6B $\cdots$ O6 <sup>iii</sup>	0.91	2.07	2.943 (3)	160

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O1 <i>W</i> —H1 <i>WA</i> ···O1	0.86	2.56	3.088 (3)	121
O1 <i>W</i> —H1 <i>WA</i> ···O2	0.86	2.00	2.795 (3)	154
O1 <i>W</i> —H1 <i>WB</i> ···O3 <sup>ii</sup>	0.86	1.91	2.757 (3)	170
O2 <i>W</i> —H2 <i>WA</i> ···O7 <sup>i</sup>	0.87	1.80	2.663 (3)	169
O2 <i>W</i> —H2 <i>WB</i> ···O6 <sup>iii</sup>	0.87	1.90	2.742 (3)	160

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