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

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The asymmetric unit of the title compound, trans-diaqua(1,4,8,11-tetraazaundecane-κ4N1,N4,N8,N11)nickel(II) bis(pyridine-2,6-dicarboxylato-κ3O2,N,O6)nickel(II) \[[\text{Ni}(L)(\text{H}_2\text{O})_2][\text{Ni}(\text{pdc})_2]\] where \(L = 1,4,8,11\text{-tetraazaundecane (C}_{12}\text{H}_{20}\text{N}_4}\) and \(\text{pdc} = \text{the dianion of pyridine-2,6-dicarboxylic acid (C}_7\text{H}_3\text{NO}_4^{2-})\) consists of an [\text{Ni}(L)(\text{H}_2\text{O})_2]^{2+} \text{complex cation and a } [\text{Ni}(\text{pdc})_2]^{2-} \text{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) Å 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 Ni^{II} ion is coordinated by the two tridentate pdc^{2-} ligands via their carboxylate and nitrogen atom donors in a distorted octahedral trans-NiO_4N_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^{2-} 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, C_{10}H_{24}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 (C_{12}H_{20}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+} \text{cation with azide (Escuer et al., 1993), cyanide (Koo et al., 2003), andcyanometalate (Koo et al., 2003; Shek et al., 2005; Talukder et al.,...
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, Tsymbal et al., 2021), coordination polymers based on its structural analogue, pyridine-2,6-dicarboxylate (C₇H₃NO₄⁻; pdc²⁻), are confined to a sole example (Choi et al., 2003). Interestingly, an attempt to prepare a coordination polymer containing the [Ni(cyclam)]²⁺ cation with pdc²⁻ led to the ionic product [Ni(cyclam)(H₂O)₂][Ni(pdc)₂]·2.5H₂O 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 tetraaza cations and aromatic carboxylates, we report here the reaction of nickel(II) with this chelating ligand (Park et al., 2007). Interestingly, an attempt to prepare a coordination polymer containing the [Ni(cyclam)]²⁺ cation with pdc²⁻ led to the ionic product [Ni(cyclam)(H₂O)₂][Ni(pdc)₂]·2.5H₂O 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)]²⁺ with pdc²⁻, namely [trans-diaqua(1,4,8,11-tetraazaundecane-k⁴N¹N⁴N⁷N₁₀)nickel(II)][bis(pyridine-2,6-dicarboxylato-k²N,O,O)nickel(II)], [Ni(L)(H₂O)₂][Ni(pdc)₂]. I. Similar to the reaction of pyridine-2,6-dicarboxylate with the [Ni(cyclam)]²⁺ 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)₂]²⁻ 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.

### Structural commentary

The molecular structure of the title compound I is shown in Fig. 1. Atom NiI is coordinated by the two tridentate pdc²⁻ ligands via their carboxylate and nitrogen donors, resulting in the formation of the [Ni(pdc)₂]²⁻ divalent anion, which is charge-balanced by the [Ni(L)(H₂O)₂]²⁺ divalent cation formed by atom Ni2.

The coordination polyhedron of NiII in the complex anion can be described as a tetragonally compressed trans-NiO₄N₂ 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 carboxyl 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 pdc²⁻ carboxylate rings are oriented nearly orthogonally with an angle of 81.5 (3)° between their mean planes.

The NiII 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-NiO₄N₂ 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...
the trans-III configuration usually observed in cyclam complexes (Bosnich et al., 1965). This conformation is also characteristic of the macrocyclic ligand in [Ni(cyclam)-(H₂O)₂]²⁺ (Park et al., 2007), although the bite angles in the five-membered (85.54°/C₁₄) and six-membered (94.46°/C₁₄) chelate rings are correspondingly larger and smaller compared to those in I (Table 1).

3. Supramolecular features

The crystals of I are composed of [Ni(L)(H₂O)₂]²⁺ complex cations and [Ni(pdc)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 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-

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

| D—H · · · A   | D—H | H · · · A | D · · · A | D—H · · · A |
|---------------|------|----------|----------|------------|
| N3—H3A···O8   | 0.91 | 2.41     | 3.213 (3)| 147        |
| N3—H3B···O4   | 0.91 | 2.11     | 3.015 (3)| 176        |
| N4—H4A···O1   | 1.00 | 2.07     | 3.054 (3)| 167        |
| N5—H5A···O2   | 1.00 | 2.08     | 3.054 (3)| 163        |
| N6—H6A···O3   | 0.91 | 2.14     | 2.986 (3)| 154        |
| N6—H6B···O6   | 0.91 | 2.07     | 2.943 (3)| 160        |
| O1W···H1WA···O1 | 0.86 | 2.56   | 3.088 (3)| 121        |
| O1W···H1WA···O2 | 0.86 | 2.00   | 2.793 (3)| 154        |
| O1W···H1WB···O3 | 0.86 | 1.91   | 2.757 (3)| 170        |
| O2W···H2WA···O7 | 0.87 | 1.80   | 2.663 (3)| 169        |
| O2W···H2WB···O6 | 0.87 | 1.90   | 2.742 (3)| 160        |

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

Figure 2
Nearest surroundings of the cation in I formed by hydrogen bonding (dotted lines). [Symmetry codes: (i) x−1, y, z; (ii) −x+2, y−1/z+1; (iii) −x+1, y−1/z+1]

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−1/z−1; (iii) −x+1, y−1/z−1]

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(C2H3N4)2(H2O)]2- | [Ni(C2H3N4)2]- |
| M, g/mol | 643.93 |
| Crystal system, space group | Orthorhombic, P21/21 |
| Temperature (K) | 100 |
| a, b, c (Å) | 9.3219 (6), 16.3211 (10), 16.9483 (8) |
| V (Å³) | 2578.6 (3) |
| Z | 4 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 1.53 |
| Crystal size (mm) | 0.25 x 0.2 x 0.2 |

| Data collection | Diffractometer | Bruker APEXII CCD |
|-----------------|---------------|------------------|
| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2019) |
| Tmin, Tmax | 0.705, 0.737 |
| No. of measured, independent and observed | 36128, 4909, 4668 |
| Rint | 0.045 |
| δαmax(Å⁻¹) | 0.610 |

| Refinement | R(F² > 2σ(F²)), wR(F²), S |
|------------|----------------------------|
| No. of reflections | 4909 |
| No. of parameters | 356 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| Δρmax, Δρmin (e Å⁻³) | 0.49, -0.26 |
| Absolute structure | Flack x determined using 1953 quotients [(F’)−(F’)]/[(F’)+(F’)] (Parsons et al., 2013) |
| Absolute structure parameter | −0.010 (4) |

Computer programs: CrysAlis PRO (Rigaku OD, 2019), SHELXTL2018/2 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), Mercury (Macrae et al., 2020) and pubICIF (Westrup, 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)(H₂O)]²⁺ cation have been structurally characterized to date, the closest analogue being the complex [Ni(L)](ClO₄)₂ (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 (2.18 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)(H₂O)]²⁺ in I and [Ni(cyclam)(H₂O)]₂²⁺ 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)](ClO₄)₂ was prepared by mixing equimolarmount of L and nickel perchlorate hexahydrate in ethanol. The title compound I was prepared as follows. A solution of [Ni(L)](ClO₄)₂ (11 mg, 0.026 mmol) in 1 ml of DMF was added to 0.4 ml of an aqueous solution of Na₂(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 C₂₁H₁₈N₄Na₂O₁₀: 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 Å (primary amino groups) or 1.00 Å (secondary aminogroups) with Ueq(H) values of 1.2Ueq of the parent atoms. Water H atoms were positioned geometrically (O—H = 0.71–0.85 Å) and refined as riding with Ueq(H) = 1.5Ueq(O).

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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-κ⁴N¹,N⁴,N⁸,N¹¹)nickel(II) bis(pyridine-2,6-dicarboxylato-κ³O²,N,O⁶)nickel(II)

Crystal data

[Ni(C₇H₂₀N₄)(H₂O)₂][Ni(C₇H₃NO₄)₂]

\[M_r = 643.93\]

Orthorhombic, \(P2₁2₁2₁\)

\(a = 9.3219\) (6) Å

\(b = 16.3211\) (10) Å

\(c = 16.9483\) (8) Å

\(V = 2578.6\) (3) Å³

\(Z = 4\)

\(F(000) = 1336\)

Data collection

Bruker APEXII CCD diffractometer

Radiation source: fine-focus sealed tube

\(\varphi\) and \(\omega\) scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2019)

\(T_{\text{min}} = 0.705, T_{\text{max}} = 0.737\)

36128 measured reflections

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 \(P = (F_o^2 + 2F_c^2)/3\)

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

\(\Delta\rho_{\text{max}} = 0.49\) e Å⁻³

\(\Delta\rho_{\text{min}} = -0.26\) e Å⁻³

\(D_x = 1.659\) Mg m⁻³

Mo \(K\alpha\) radiation, \(\lambda = 0.71073\) Å

Cell parameters from 8341 reflections

\(\theta = 2.5–25.3^\circ\)

\(\mu = 1.53\) mm⁻¹

\(T = 100\) K

Prism, clear light pink

0.25 × 0.2 × 0.2 mm

4909 independent reflections

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

\(R_{\text{int}} = 0.045\)

\(\theta_{\text{max}} = 25.7^\circ, \theta_{\text{min}} = 2.4^\circ\)

\(h = -11\rightarrow11\)

\(k = -19\rightarrow19\)

\(l = -20\rightarrow20\)
Absolute structure: Flack $x$ determined using 1953 quotients $[(I^-)-(I^+)]/[(I^+)+(I^-)]$ (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 ($\AA^2$)

|    | $x$      | $y$         | $z$          | $U_{iso}$/$U_{eq}$ |
|----|----------|-------------|--------------|---------------------|
| Ni1| 1.09379  | 0.79146 (2) | 0.79300 (2)  | 0.01132 (9)        |
| O1 | 0.9734   | 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)*        |
### Atomic displacement parameters (Å²)

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| 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)|
### Geometric parameters (Å, °)

|          | Ni1—O1    | Ni1—O3    | Ni1—O5    | Ni1—O7    | Ni1—N1    | Ni1—N2    | Ni1—N3    | Ni1—N4    | Ni1—N5    | Ni1—N6    |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 2.099 (2)| 2.109 (2) | 2.111 (2) | 2.1343 (19)| 1.961 (2) | 1.969 (2) | 1.980 (2) | 2.074 (2) | 2.088 (2) | 2.095 (2) | 2.089 (3) |
| O1—C1   | 1.264 (4) | O2W—H2WA | O2—H2WA  | 1.264 (4) | 1.251 (4) | 1.221 (4) | 1.289 (2) | 0.8563    | 0.8593    | 0.8743    |
| O3—C7   | 1.294 (3) | 1.245 (3) | 1.224 (3) | 1.294 (3) | 1.251 (4) | 1.221 (4) | 1.282 (3) | 0.8744    | 1.475 (4) | 1.483 (4) |
| O2—C1   | 1.251 (4) | 1.221 (4) | 1.262 (3) | 1.282 (3) | 1.245 (3) | 1.235 (4) | 1.334 (4) | 1.477 (4) | 1.0000    | 1.0000    |
| O6—C8   | 1.336 (4) | 1.336 (4) | 1.336 (4) | 1.336 (4) | 1.336 (4) | 1.336 (4) | 1.336 (4) | 1.336 (4) | 1.336 (4) | 1.336 (4) |
| Bond          | Bond Length (Å) | Bond Length (Å) | Bond Length (Å) |
|---------------|-----------------|-----------------|-----------------|
| 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)     |
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 177.3 (3)
Ni1—O3—C7—C6 −5.5 (3)  C4—C5—C6—C7 −174.5 (3)
Ni1—O5—C8—O6 179.7 (2)  C5—C6—N1—C2 −179.3 (2)
Ni1—O5—C8—C9 −2.3 (3)  C5—C6—N1—C6 −177.8 (2)
Ni1—O7—C14—O8 171.5 (2)  C6—N1—C2—C1 4.6 (3)
Ni1—O7—C14—C13 −10.1 (3)  C6—N1—C2—C3 175.4 (2)
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—H21A 164.3 (3)
N1—C6—C7—O3 4.6 (4)  Ni2—N6—C21—H21B 164.3 (3)
N1—C6—C7—O4 −175.8 (3)  Ni2—C16—N4—C17 176.1 (3)
N2—C9—C10—C11 −0.4 (4)  N5—C20—C21—C19 65.8 (4)
N2—C13—C14—O7 6.8 (4)  N5—C20—C21—C20 176.1 (3)
N2—C13—C14—O8 −174.7 (3)  C16—N4—C17—C18 176.1 (3)
C1—C2—C3—C4 177.0 (3)  C17—N4—C16—C15 176.1 (3)
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, °)

| D—H···A   | D—H | H···A | D····A   | D—H···A |
|-----------|-----|-------|----------|---------|
| N3—H3A···O8i | 0.91 | 2.41  | 3.213 (3) | 147     |
| N3—H3B···O4ii | 0.91 | 2.11  | 3.015 (3) | 176     |
| N4—H4A···O1 | 1.00 | 2.07  | 3.054 (3) | 167     |
| N5—H5A···O2 | 1.00 | 2.08  | 3.054 (3) | 163     |
| N6—H6A···O3ii | 0.91 | 2.14  | 2.986 (3) | 154     |
| N6—H6B···O6iii | 0.91 | 2.07  | 2.943 (3) | 160     |
|            | d (Å) | r (Å)  | D (Å)     | θ (°) |
|------------|-------|--------|-----------|-------|
| O1W—H1WA···O1 | 0.86  | 2.56   | 3.088 (3) | 121   |
| O1W—H1WA···O2 | 0.86  | 2.00   | 2.795 (3) | 154   |
| O1W—H1WB···O3ii | 0.86  | 1.91   | 2.757 (3) | 170   |
| O2W—H2WA···O7i | 0.87  | 1.80   | 2.663 (3) | 169   |
| O2W—H2WB···O6ii | 0.87  | 1.90   | 2.742 (3) | 160   |

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.