Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# Propane-1,2-diammonium bis(pyridine-2,6-dicarboxylato-$\kappa^3O,N,O'$)nickelate(II) tetrahydrate

**Hossein Aghabozorg,[a]* Mohammad Heidari,[a] Sara Bagheri,[b] Jafar Attar Gharamaleki[a] and Mohammad Ghadermazi[c]**

[a]Faculty of Chemistry, Tarbiat Moallem University, 49 Mofateh Avenue, Tehran, Iran, [b]Department of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran, and [c]Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj, Iran
Correspondence e-mail: haghabozorg@yahoo.com

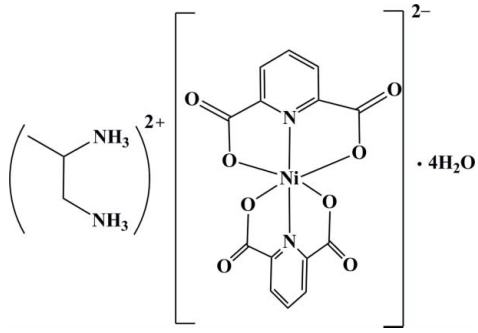
Received 28 April 2008; accepted 29 May 2008

Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.024; $wR$ factor = 0.060; data-to-parameter ratio = 20.6.

The reaction of nickel(II) nitrate hexahydrate, propane-1,2-diamine and pyridine-2,6-dicarboxylic acid in a 1:2:2 molar ratio in aqueous solution resulted in the formation of the title compound, $(C_3H_{12}N_2)[Ni(C_7H_3NO_4)_2]\cdot 4H_2O$ or ($p$-1,2-da$H_2$)-[Ni(pydc)$_2$]·4$H_2O$ (where $p$-1,2-da is propane-1,2-diamine and pydc$H_2$ is pyridine-2,6-dicarboxylic acid). The geometry of the resulting $NiN_2O_4$ coordination can be described as distorted octahedral. Considerable C═O$\cdots\pi$ stacking interactions are observed between the carboxylate C═O groups and the pyridine rings of the $(pydc)^{2-}$ fragments, with O$\cdots\pi$ distances of 3.1563 (12) and 3.2523 (12) Å and C═O$\cdots\pi$ angles of 95.14 (8) and 94.64 (8)°. In the crystal structure, a wide range of non-covalent interactions, consisting of hydrogen bonding [O—H$\cdots$O, N—H$\cdots$O and C—H$\cdots$O, with $D\cdots A$ distances ranging from 2.712 (2) to 3.484 (2) Å], ion pairing, $\pi$–$\pi$ [centroid-to-centroid distance = 3.4825 (8) Å] and C═O$\cdots\pi$ stacking, connect the various components to form a supramolecular structure.

## Related literature

For related literature, see: Aghabozorg *et al.* (2007); Aghabozorg, Ghadermazi & Attar Gharamaleki (2006); Aghabozorg, Ghadermazi & Ramezanipour (2006); Aghabozorg, Heidari *et al.* (2008); Aghabozorg, Manteghi & Sheshmani (2008).




## Experimental

### Crystal data

$(C_3H_{12}N_2)[Ni(C_7H_3NO_4)_2]\cdot 4H_2O$
$M_r$ = 537.13
Orthorhombic, $Pna2_1$
$a$ = 20.7598 (6) Å
$b$ = 8.2582 (2) Å
$c$ = 12.7242 (4) Å
$V$ = 2181.42 (11) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.96 mm$^{-1}$
$T$ = 100 (2) K
0.26 × 0.22 × 0.11 mm

### Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.781, $T_{max}$ = 0.898
36654 measured reflections
6379 independent reflections
6016 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.035

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.059
$S$ = 1.01
6379 reflections
310 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.34 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.33 e Å$^{-3}$
Absolute structure: Flack (1983), 2846 Friedel pairs
Flack parameter: 0.004 (7)

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O1$W$—H1$WA\cdots$O4$W$ | 0.82 | 1.97 | 2.788 (2) | 173 |
| O1$W$—H1$WB\cdots$O2 | 0.82 | 2.47 | 3.109 (2) | 135 |
| O1$W$—H1$WB\cdots$O6 | 0.82 | 2.21 | 2.912 (2) | 144 |
| O2$W$—H2$WA\cdots$O3 | 0.82 | 2.21 | 2.759 (2) | 125 |
| N3—H3$B\cdots$O4$^{i}$ | 0.91 | 1.90 | 2.795 (2) | 168 |
| N3—H3$C\cdots$O1$W$ | 0.91 | 1.91 | 2.763 (2) | 155 |
| N3—H3$D\cdots$O8$^{ii}$ | 0.91 | 1.88 | 2.783 (2) | 176 |
| O2$W$—H2$WB\cdots$O1$^{iii}$ | 0.82 | 2.07 | 2.849 (2) | 160 |
| N4—H4$B\cdots$O3$W^{ii}$ | 0.91 | 1.92 | 2.812 (2) | 165 |
| N4—H4$C\cdots$O1 | 0.91 | 1.92 | 2.813 (2) | 168 |
| N4—H4$D\cdots$O4$W^{iv}$ | 0.91 | 1.91 | 2.777 (2) | 160 |
| O3$W$—H3$WA\cdots$O8 | 0.82 | 2.03 | 2.771 (2) | 149 |
| O3$W$—H3$WB\cdots$O4$^{v}$ | 0.82 | 1.99 | 2.787 (2) | 166 |
| O4$W$—H4$WA\cdots$O2$W^{i}$ | 0.82 | 1.99 | 2.749 (2) | 153 |
| O4$W$—H4$WB\cdots$O5 | 0.82 | 1.90 | 2.712 (2) | 171 |
| C10—H10$A\cdots$O6$^{vi}$ | 0.95 | 2.54 | 3.289 (2) | 136 |
| C11—H11$A\cdots$O1$W^{vi}$ | 0.95 | 2.58 | 3.484 (2) | 160 |
| C15—H15$B\cdots$O5$^{vii}$ | 0.99 | 2.30 | 3.268 (2) | 164 |
| C16—H16$A\cdots$O7$^{ii}$ | 1.00 | 2.49 | 3.291 (2) | 137 |

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); 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: SU2054).

## References


Aghabozorg, H., Ghadermazi, M. & Attar Gharamaleki, J. (2006). *Acta Cryst.* E**62**, o3174–o3176.

Aghabozorg, H., Ghadermazi, M. & Ramezanipour, F. (2006). *Acta Cryst.* E**62**, o1143–o1146.

Aghabozorg, H., Ghadermazi, M., Sheshmani, S. & Attar Gharamaleki, J. (2007). *Acta Cryst.* E**63**, o2985–o2986.

Aghabozorg, H., Heidari, M., Ghadermazi, M. & Attar Gharamaleki, J. (2008). *Acta Cryst.* E**64**, o1045–o1046.

Aghabozorg, H., Manteghi, F. & Sheshmani, S. (2008). *J. Iran. Chem. Soc.* **5**, 184–227.

Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

*Acta Cryst.* (2008). E**64**, m874–m875 [doi:10.1107/S1600536808016309]

# Propane-1,2-diammonium bis(pyridine-2,6-dicarboxylato-$\kappa^3O,N,O'$)nickelate(II) tetrahydrate

**Hossein Aghabozorg, Mohammad Heidari, Sara Bagheri, Jafar Attar Gharamaleki and Mohammad Ghadermazi**

## S1. Comment

Recently, we have defined a plan to prepare water soluble proton transfer compounds as novel self-assembled systems that can function as suitable ligands in the synthesis of metal complexes. In this regard, we have reported cases in which proton transfers from pyridine-2,6-dicarboxylic acid ($pydcH_2$), and benzene-1,2,4,5-tetracarboxylic acid ($btcH_4$), to propane-1,3-diamine (pda), propane-1,2-diamine (*p*-1,2-da) and 1,10-phenanthroline, (phen). This work has resulted in the formation of some novel proton transfer compounds such as $(pdaH_2)(pydc).(pydcH_2).2.5H_2O$ (Aghabozorg, Ghadermazi & Ramezanipour, 2006), $(pdaH_2)_2(btc).2H_2O$ (Aghabozorg *et al.*, 2007), $(p\text{-}1,2\text{-}daH_2)(pydcH)_2.2H_2O$ (Aghabozorg, Heidari *et al.*, 2008) and $(phenH)_4(btcH_3)_2(btcH_2)$ (Aghabozorg, Ghadermazi & Attar Gharamaleki, 2006). For more details and related literature see our recent review article (Aghabozorg, Manteghi & Sheshmani, 2008).

The molecular structure and crystal packing diagram of the title compound are presented in Figs. 1 and 2, respectively. The $Ni^{II}$ atom is six-coordinated by two pyridine-2,6-dicarboxylate, or $(pydc)^{2-}$, groups, *i.e.* each $(pydc)^{2-}$ ligand is coordinated through one pyridine N atom and two carboxylate O atoms. As it can be seen, atoms N1 and N2 of the two $(pydc)^{2-}$ fragments occupy the axial positions, while atoms O2, O3, O6 and O7 form the equatorial plane [with Ni—O distances ranging from 2.1178 (11) to 2.1477 (10) Å]. The N1—Ni1—N2 angle [176.17 (5)°] deviates from linearity. Therefore, the geometry of the resulting $NiN_2O_4$ coordination can be described as distorted octahedral. The O2—Ni1—O6 and O3—Ni1—O7 bond angles are equal to 87.26 (4)° and 90.55 (4)°, respectively. On the other hand, the torsion angles O3—Ni1—O7—C14 and O7—Ni1—O3—C7 are 92.68 (10)° and 95.05 (10)°, respectively, indicating that the two $(pydc)^{2-}$ units are almost perpendicular to one another. The O2—Ni1—O3 [155.41 (4)°] and O6—Ni1—O7 [155.96 (4)°] bond angles indicate that the four carboxylate groups of the two dianions are oriented in a flattened tetrahedral arrangement around the Ni1 atom.

It is interesting to note that the crystal packing shows a layered structure. The space between the layers of $[Ni(pydc)_2]^{2-}$ units is occupied by $(p\text{-}1,2\text{-}daH_2)^{2+}$ cations and uncoordinated water molecules, which bridge the $[Ni(pydc)_2]^{2-}$ units *via* hydrogen bonds (Fig 3 and Table 1). A noticeable feature of the title compound is the presence of C═O···$\pi$ stacking interactions, between C═O groups of the carboxylate with aromatic rings of pyridine-2,6-dicarboxylate, with O···$\pi$ distances of 3.1563 (12) Å for C13–O5···*Cg*1 (1/2 - *x*, 1/2 + *y*, -1/2 + *z*) and 3.2523 (12) Å for C6–O1···*Cg*2 (1/2 - *x*, -1/2 + *y*, 1/2 + *z*) [*Cg*1 and *Cg*2 are the centroids of the rings N1/C1–C5 and N2/C8–C12, respectively]. There is also considerable $\pi$–$\pi$ stacking interactions between the two aromatic rings of the $(pydc)^{2-}$ units, with a centorid–centroid distance of 3.4825 (8) Å (1/2 - *x*, -1/2 + *y*, -1/2 + *z*) [see Fig. 4]. In the crystal structure, a wide range of non-covalent interactions consisting of hydrogen bonding (of the type O—H···O, N—H···O and C—H···O with D···A ranging from 2.712 (2) Å to 3.484 (2) Å), ion pairing, $\pi$···$\pi$ and C═O···$\pi$ stacking connect the various components to form a

supramolecular structure.

## S2. Experimental

An aqueous solution of $Ni(NO_3)_2.6H_2O$ (290 mg, 1 mmol), propane-1,2-diamine (80 mg, 2 mmol) and pyridine-2,6-dicarboxylic acid (360 mg, 2 mmol) was added to each other in a 1:2:2 molar ratio, and the reaction mixture was heated at about 40°C for 5 h. Green crystals of the title compound were obtained from the solution after four weeks at room temperature.

## S3. Refinement

The hydrogen atoms of the NH3 groups and the water molecules were located in difference Fourier maps. The H(C) atom positions were included in calculated positions and treated as riding atoms with $U_{iso}$(H) = 1.2$U_{eq}$(parent C or O atoms) and 1.5$U_{eq}$(parent N or C-methyl atoms).

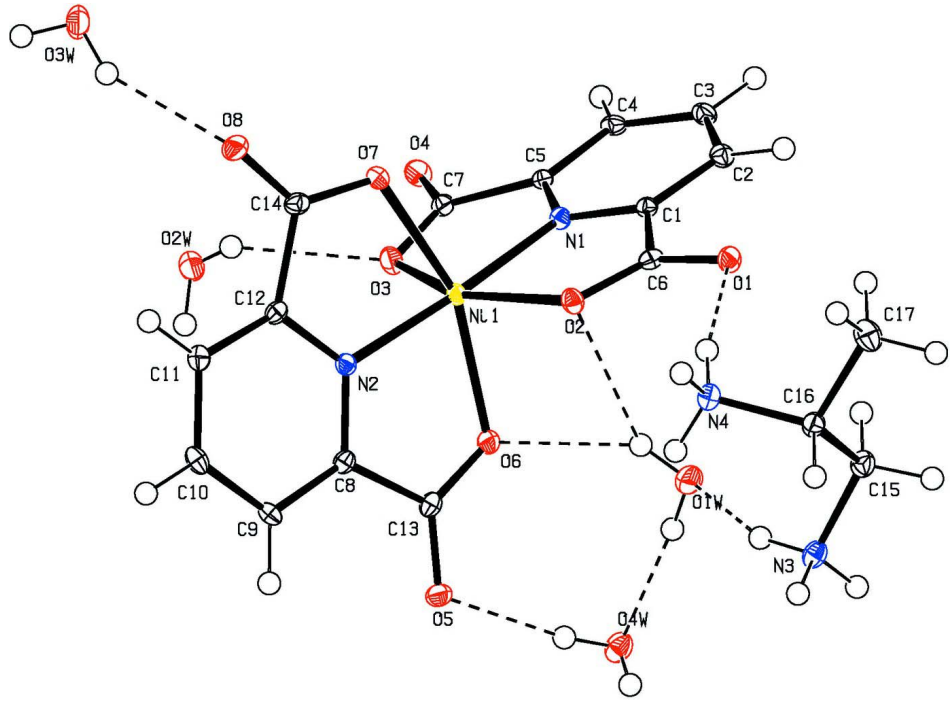



**Figure 1**

The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

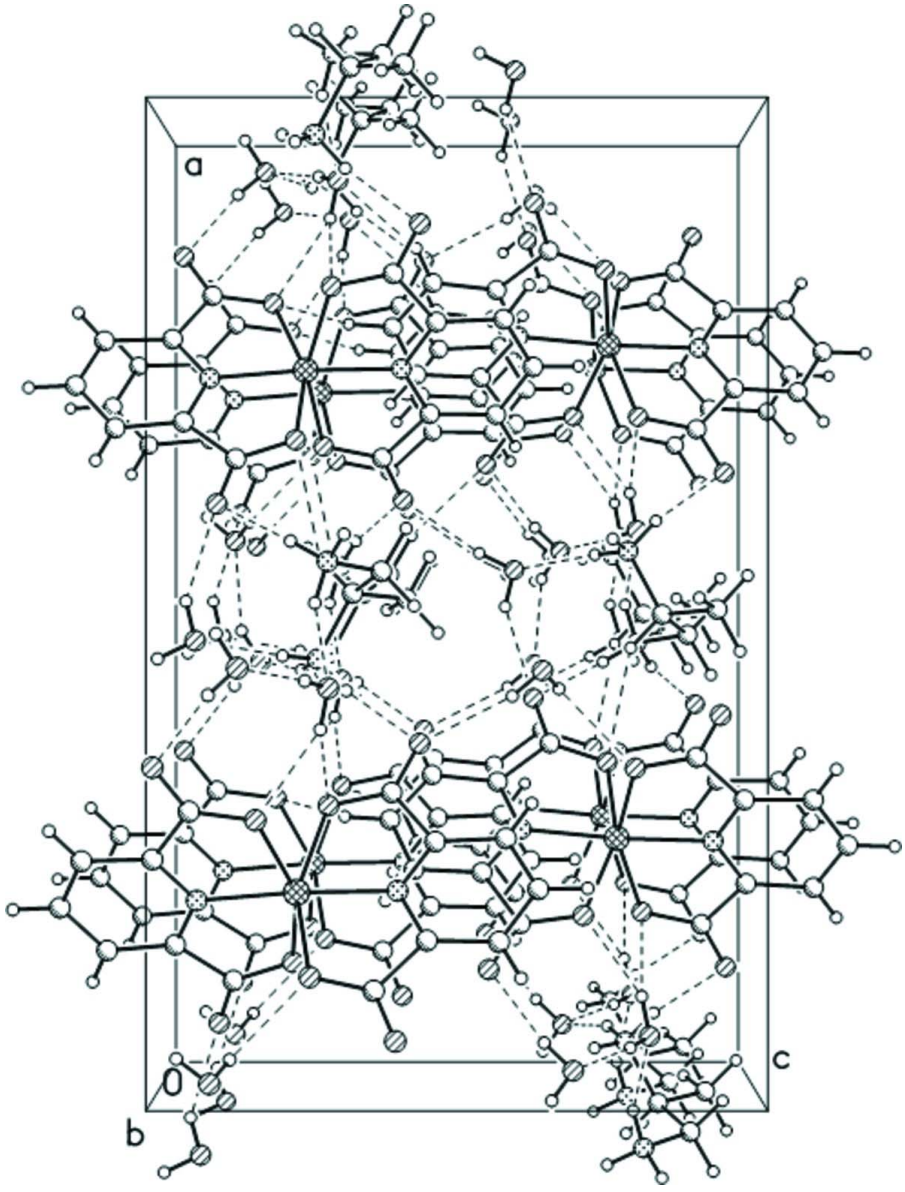



**Figure 2**

The crystal packing of the title compound as viewed approximately down *b*, with the hydrogen bonds shown as dashed lines.

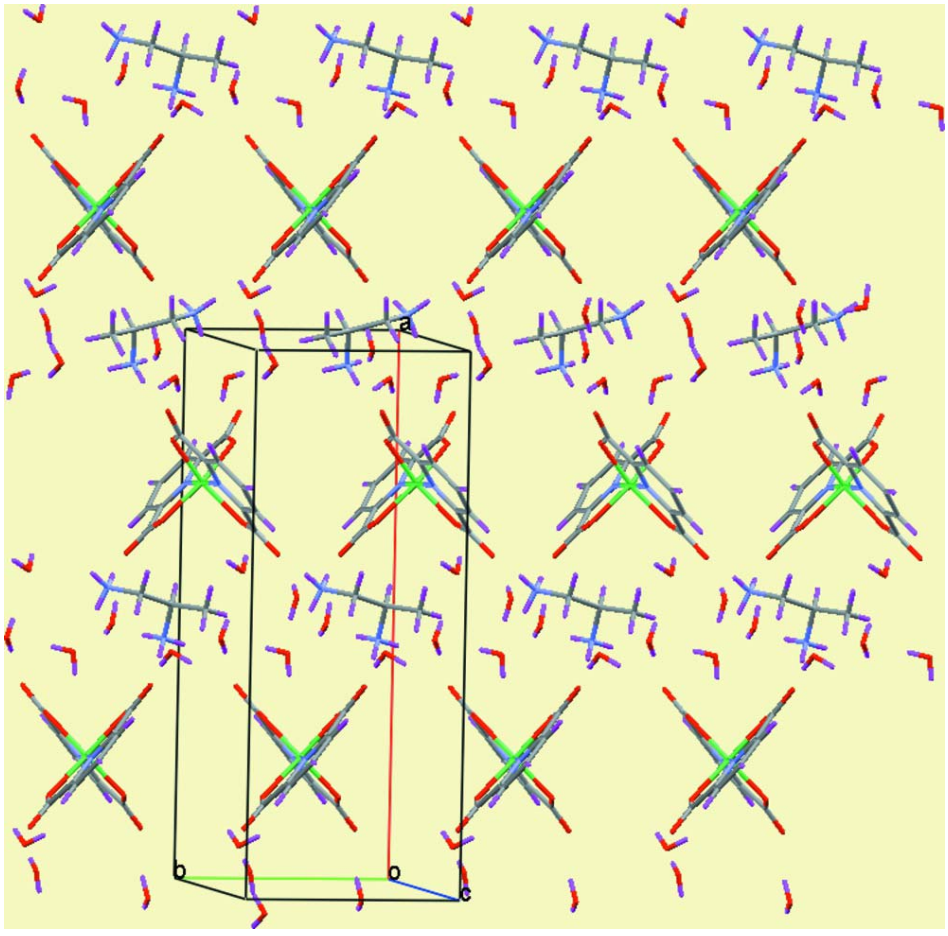



**Figure 3**

A layered packing diagram of the title compound. The space between the two layers of $[Ni(pydc)_2]^{2-}$ fragments is filled with a layer of $(p\text{-}1,2\text{-}daH_2)^{2+}$ cations and water molecules.

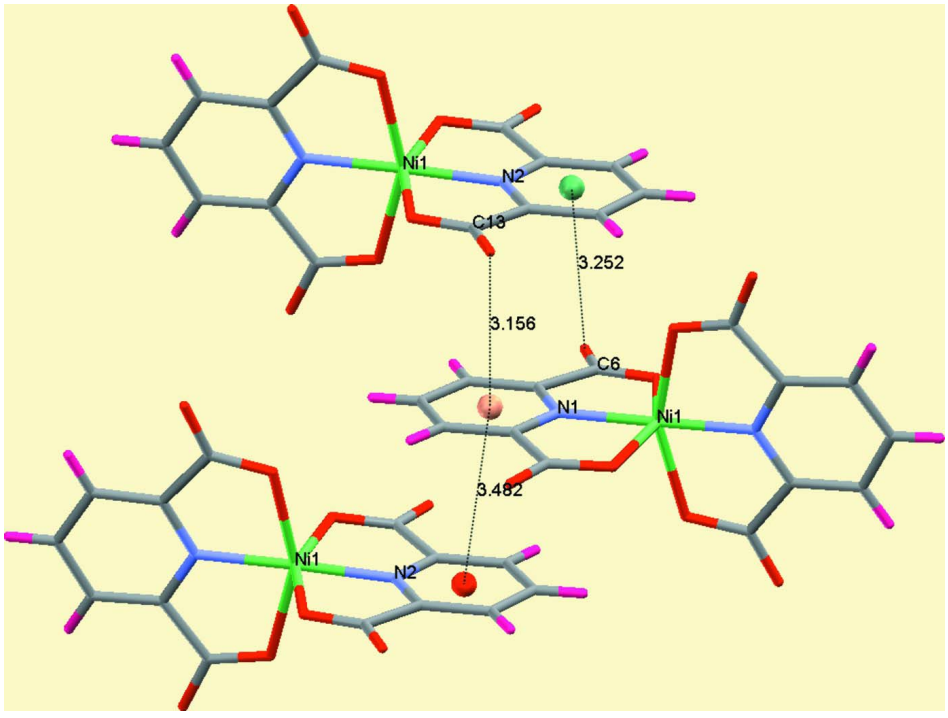



**Figure 4**

$\pi$–$\pi$ Stacking interaction between two aromatic rings of $(pydc)^{2-}$ units, with centorid–centroid distance of 3.4825 (8) Å (1/2 - *x*, -1/2 + *y*, -1/2 + *z*); C–O···$\pi$ Stacking interactions between C═O groups of carboxylate and the aromatic rings of pyridine-2,6-dicarboxylate with O···$\pi$ distances of 3.1563 (12) Å for C13—O5···*Cg*1 (1/2 - *x*, 1/2 + *y*, -1/2 + *z*) and 3.2523 (12) Å for C6—O1···*Cg*2 (1/2 - *x*, -1/2 + *y*, 1/2 + *z*) [*Cg*1 and *Cg*2 are the centroids for rings N1/C1–C5 and N2/C8–C12, respectively].

## Propane-1,2-diammonium bis(pyridine-2,6-dicarboxylato-$\kappa^3$O,N,O′)nickelate(II) tetrahydrate

*Crystal data*

$(C_3H_{12}N_2)[Ni(C_7H_3NO_4)_2]\cdot 4H_2O$
$M_r = 537.13$
Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
$a = 20.7598$ (6) Å
$b = 8.2582$ (2) Å
$c = 12.7242$ (4) Å
$V = 2181.42$ (11) Å$^3$
$Z = 4$
$F(000) = 1120$
$D_x = 1.635$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 410 reflections
$\theta = 3$–29°
$\mu = 0.96$ mm$^{-1}$
$T = 100$ K
Prism, light-green
0.26 × 0.22 × 0.11 mm

*Data collection*

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.781$, $T_{max} = 0.898$
36654 measured reflections
6379 independent reflections
6016 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 30.0°$, $\theta_{min} = 2.0°$
$h = -29\rightarrow29$
$k = -11\rightarrow11$
$l = -17\rightarrow17$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.059$
$S = 1.01$
6379 reflections
310 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.34$ e Å$^{-3}$
$\Delta\rho_{min} = -0.33$ e Å$^{-3}$
Absolute structure: Flack (1983), with how many Friedel pairs?
Absolute structure parameter: 0.004 (7)

*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 | 0.230880 (7) | 0.50781 (2) | 0.25665 (2) | 0.00841 (4) |
| O1 | 0.36657 (5) | 0.27840 (12) | 0.44207 (8) | 0.0123 (2) |
| O2 | 0.30848 (5) | 0.35043 (12) | 0.30169 (8) | 0.0110 (2) |
| O3 | 0.15872 (5) | 0.68763 (13) | 0.28120 (8) | 0.0131 (2) |
| O4 | 0.10593 (5) | 0.81657 (13) | 0.41025 (9) | 0.0133 (2) |
| O5 | 0.35128 (5) | 0.74395 (13) | 0.04995 (8) | 0.0128 (2) |
| O6 | 0.30178 (5) | 0.66991 (13) | 0.19960 (8) | 0.0113 (2) |
| O7 | 0.15889 (5) | 0.32530 (12) | 0.24551 (9) | 0.0120 (2) |
| O8 | 0.09570 (5) | 0.20477 (13) | 0.12645 (9) | 0.0146 (2) |
| N1 | 0.23302 (5) | 0.53498 (17) | 0.41041 (11) | 0.0085 (2) |
| N2 | 0.22246 (6) | 0.48264 (15) | 0.10356 (12) | 0.0090 (3) |
| C1 | 0.27701 (7) | 0.45504 (17) | 0.46722 (12) | 0.0087 (2) |
| C2 | 0.28041 (8) | 0.47344 (19) | 0.57519 (13) | 0.0109 (3) |
| H2A | 0.3120 | 0.4178 | 0.6153 | 0.013* |
| C3 | 0.23594 (7) | 0.57630 (18) | 0.62343 (12) | 0.0112 (3) |
| H3A | 0.2371 | 0.5909 | 0.6975 | 0.013* |
| C4 | 0.18997 (7) | 0.65754 (17) | 0.56366 (11) | 0.0102 (3) |
| H4A | 0.1593 | 0.7270 | 0.5958 | 0.012* |
| C5 | 0.19040 (7) | 0.63384 (17) | 0.45558 (11) | 0.0088 (2) |
| C6 | 0.32098 (6) | 0.35197 (16) | 0.39952 (12) | 0.0096 (2) |
| C7 | 0.14761 (7) | 0.71970 (17) | 0.37710 (11) | 0.0102 (3) |
| C8 | 0.26305 (6) | 0.56135 (18) | 0.04015 (12) | 0.0095 (3) |
| C9 | 0.26076 (7) | 0.5380 (2) | −0.06858 (12) | 0.0105 (3) |

| | | | | |
|---|---|---|---|---|
| H9A | 0.2901 | 0.5919 | −0.1140 | 0.013* |
| C10 | 0.21417 (7) | 0.43328 (18) | −0.10826 (11) | 0.0121 (3) |
| H10A | 0.2116 | 0.4147 | −0.1818 | 0.015* |
| C11 | 0.17109 (7) | 0.35526 (17) | −0.04071 (12) | 0.0110 (3) |
| H11A | 0.1385 | 0.2857 | −0.0673 | 0.013* |
| C12 | 0.17748 (6) | 0.38260 (17) | 0.06599 (12) | 0.0097 (2) |
| C13 | 0.30969 (6) | 0.66803 (17) | 0.10021 (12) | 0.0101 (3) |
| C14 | 0.14033 (7) | 0.29812 (17) | 0.15243 (12) | 0.0108 (3) |
| N3 | 0.54006 (6) | 0.43977 (15) | 0.30200 (10) | 0.0123 (2) |
| H3B | 0.5651 | 0.5201 | 0.3289 | 0.018* |
| H3C | 0.5010 | 0.4809 | 0.2837 | 0.018* |
| H3D | 0.5595 | 0.3971 | 0.2442 | 0.018* |
| N4 | 0.44676 (5) | 0.16524 (15) | 0.27970 (10) | 0.0118 (2) |
| H4B | 0.4502 | 0.2393 | 0.2270 | 0.018* |
| H4C | 0.4162 | 0.1982 | 0.3263 | 0.018* |
| H4D | 0.4354 | 0.0676 | 0.2523 | 0.018* |
| C15 | 0.53120 (7) | 0.31041 (17) | 0.38271 (12) | 0.0130 (3) |
| H15A | 0.4983 | 0.3459 | 0.4340 | 0.016* |
| H15B | 0.5722 | 0.2949 | 0.4212 | 0.016* |
| C16 | 0.51052 (7) | 0.14977 (17) | 0.33504 (12) | 0.0113 (2) |
| H16A | 0.5437 | 0.1154 | 0.2827 | 0.014* |
| C17 | 0.50526 (8) | 0.01962 (18) | 0.41937 (13) | 0.0174 (3) |
| H17A | 0.4940 | −0.0840 | 0.3866 | 0.026* |
| H17B | 0.4718 | 0.0499 | 0.4700 | 0.026* |
| H17C | 0.5466 | 0.0091 | 0.4558 | 0.026* |
| O1W | 0.42220 (5) | 0.59529 (14) | 0.30653 (9) | 0.0169 (2) |
| H1WA | 0.4295 | 0.6786 | 0.2735 | 0.020* |
| H1WB | 0.3837 | 0.5823 | 0.2945 | 0.020* |
| O2W | 0.06395 (6) | 0.74698 (19) | 0.13415 (10) | 0.0297 (3) |
| H2WA | 0.0821 | 0.6693 | 0.1612 | 0.036* |
| H2WB | 0.0882 | 0.7755 | 0.0867 | 0.036* |
| O3W | −0.03481 (5) | 0.15335 (15) | 0.09506 (9) | 0.0199 (2) |
| H3WA | 0.0027 | 0.1743 | 0.0800 | 0.024* |
| H3WB | −0.0520 | 0.1482 | 0.0372 | 0.024* |
| O4W | 0.44262 (5) | 0.86620 (13) | 0.18005 (9) | 0.0158 (2) |
| H4WA | 0.4731 | 0.8280 | 0.1474 | 0.019* |
| H4WB | 0.4180 | 0.8294 | 0.1357 | 0.019* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.00786 (7) | 0.01104 (7) | 0.00634 (7) | 0.00044 (6) | −0.00030 (7) | −0.00050 (7) |
| O1 | 0.0097 (4) | 0.0146 (5) | 0.0125 (5) | 0.0032 (4) | −0.0006 (4) | 0.0011 (4) |
| O2 | 0.0123 (4) | 0.0127 (5) | 0.0082 (5) | 0.0015 (4) | −0.0003 (4) | −0.0013 (4) |
| O3 | 0.0121 (5) | 0.0174 (5) | 0.0097 (5) | 0.0037 (4) | −0.0006 (4) | 0.0003 (4) |
| O4 | 0.0125 (5) | 0.0146 (5) | 0.0129 (5) | 0.0047 (4) | 0.0020 (4) | 0.0016 (4) |
| O5 | 0.0110 (5) | 0.0154 (5) | 0.0121 (5) | −0.0025 (4) | 0.0019 (4) | −0.0005 (4) |
| O6 | 0.0106 (5) | 0.0139 (5) | 0.0092 (5) | −0.0009 (4) | −0.0003 (4) | −0.0009 (4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O7 | 0.0115 (4) | 0.0165 (4) | 0.0081 (5) | −0.0015 (3) | 0.0002 (4) | 0.0010 (4) |
| O8 | 0.0131 (5) | 0.0173 (5) | 0.0134 (5) | −0.0049 (4) | −0.0003 (4) | −0.0013 (4) |
| N1 | 0.0095 (6) | 0.0079 (5) | 0.0080 (6) | −0.0005 (4) | −0.0004 (4) | −0.0014 (5) |
| N2 | 0.0081 (5) | 0.0099 (5) | 0.0088 (6) | 0.0014 (4) | 0.0000 (5) | 0.0009 (5) |
| C1 | 0.0084 (6) | 0.0083 (6) | 0.0095 (6) | −0.0008 (5) | −0.0002 (5) | 0.0010 (5) |
| C2 | 0.0123 (6) | 0.0093 (6) | 0.0111 (7) | −0.0004 (5) | −0.0004 (5) | 0.0009 (5) |
| C3 | 0.0136 (6) | 0.0122 (6) | 0.0080 (6) | −0.0017 (5) | 0.0010 (5) | −0.0003 (5) |
| C4 | 0.0106 (6) | 0.0110 (6) | 0.0090 (6) | −0.0010 (5) | 0.0032 (5) | −0.0012 (5) |
| C5 | 0.0074 (6) | 0.0098 (6) | 0.0094 (6) | −0.0007 (5) | 0.0001 (5) | 0.0019 (5) |
| C6 | 0.0084 (6) | 0.0084 (6) | 0.0121 (6) | −0.0010 (4) | 0.0012 (5) | −0.0001 (5) |
| C7 | 0.0090 (6) | 0.0102 (6) | 0.0114 (6) | −0.0010 (5) | −0.0005 (5) | 0.0012 (5) |
| C8 | 0.0080 (6) | 0.0096 (6) | 0.0108 (7) | 0.0008 (5) | 0.0000 (5) | −0.0010 (5) |
| C9 | 0.0135 (6) | 0.0098 (6) | 0.0081 (7) | 0.0006 (5) | 0.0003 (5) | 0.0022 (5) |
| C10 | 0.0171 (7) | 0.0122 (6) | 0.0071 (6) | 0.0015 (5) | −0.0011 (5) | −0.0013 (5) |
| C11 | 0.0112 (6) | 0.0105 (6) | 0.0112 (6) | 0.0007 (5) | −0.0015 (5) | −0.0004 (5) |
| C12 | 0.0073 (6) | 0.0098 (6) | 0.0121 (6) | 0.0011 (5) | 0.0001 (5) | −0.0004 (5) |
| C13 | 0.0083 (6) | 0.0096 (6) | 0.0125 (6) | 0.0015 (5) | −0.0007 (5) | −0.0010 (5) |
| C14 | 0.0088 (6) | 0.0116 (6) | 0.0119 (6) | 0.0010 (5) | 0.0022 (5) | 0.0001 (5) |
| N3 | 0.0108 (5) | 0.0121 (5) | 0.0141 (6) | −0.0006 (4) | −0.0012 (4) | −0.0033 (5) |
| N4 | 0.0106 (5) | 0.0127 (5) | 0.0122 (6) | 0.0001 (4) | −0.0016 (4) | −0.0010 (4) |
| C15 | 0.0127 (6) | 0.0143 (6) | 0.0119 (6) | −0.0011 (5) | −0.0011 (5) | −0.0020 (5) |
| C16 | 0.0099 (6) | 0.0127 (6) | 0.0113 (6) | 0.0003 (5) | −0.0007 (5) | −0.0006 (5) |
| C17 | 0.0204 (7) | 0.0153 (7) | 0.0164 (7) | 0.0027 (5) | −0.0024 (6) | 0.0026 (6) |
| O1W | 0.0118 (5) | 0.0196 (5) | 0.0193 (6) | 0.0011 (4) | −0.0009 (4) | 0.0034 (4) |
| O2W | 0.0140 (5) | 0.0595 (9) | 0.0155 (6) | −0.0035 (6) | −0.0019 (4) | 0.0121 (6) |
| O3W | 0.0142 (5) | 0.0318 (6) | 0.0138 (5) | 0.0009 (5) | −0.0037 (4) | −0.0011 (5) |
| O4W | 0.0139 (5) | 0.0171 (5) | 0.0163 (5) | −0.0014 (4) | −0.0006 (4) | −0.0047 (4) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ni1—N2 | 1.9668 (15) | C9—H9A | 0.9500 |
| Ni1—N1 | 1.9698 (14) | C10—C11 | 1.398 (2) |
| Ni1—O6 | 2.1178 (11) | C10—H10A | 0.9500 |
| Ni1—O7 | 2.1273 (10) | C11—C12 | 1.383 (2) |
| Ni1—O3 | 2.1324 (10) | C11—H11A | 0.9500 |
| Ni1—O2 | 2.1477 (10) | C12—C14 | 1.514 (2) |
| O1—C6 | 1.2483 (17) | N3—C15 | 1.4932 (19) |
| O2—C6 | 1.2717 (18) | N3—H3B | 0.9100 |
| O3—C7 | 1.2697 (18) | N3—H3C | 0.9100 |
| O4—C7 | 1.2516 (17) | N3—H3D | 0.9100 |
| O5—C13 | 1.2441 (18) | N4—C16 | 1.5048 (17) |
| O6—C13 | 1.2754 (19) | N4—H4B | 0.9100 |
| O7—C14 | 1.2655 (19) | N4—H4C | 0.9100 |
| O8—C14 | 1.2498 (18) | N4—H4D | 0.9100 |
| N1—C5 | 1.3340 (19) | C15—C16 | 1.5205 (19) |
| N1—C1 | 1.3387 (19) | C15—H15A | 0.9900 |
| N2—C12 | 1.335 (2) | C15—H15B | 0.9900 |
| N2—C8 | 1.335 (2) | C16—C17 | 1.523 (2) |

| | | | |
|---|---|---|---|
| C1—C2 | 1.384 (2) | C16—H16A | 1.0000 |
| C1—C6 | 1.516 (2) | C17—H17A | 0.9800 |
| C2—C3 | 1.397 (2) | C17—H17B | 0.9800 |
| C2—H2A | 0.9500 | C17—H17C | 0.9800 |
| C3—C4 | 1.393 (2) | O1W—H1WA | 0.8201 |
| C3—H3A | 0.9500 | O1W—H1WB | 0.8200 |
| C4—C5 | 1.389 (2) | O2W—H2WA | 0.8201 |
| C4—H4A | 0.9500 | O2W—H2WB | 0.8198 |
| C5—C7 | 1.5130 (19) | O3W—H3WA | 0.8200 |
| C8—C9 | 1.398 (2) | O3W—H3WB | 0.8201 |
| C8—C13 | 1.516 (2) | O4W—H4WA | 0.8201 |
| C9—C10 | 1.392 (2) | O4W—H4WB | 0.8201 |

| | | | |
|---|---|---|---|
| N2—Ni1—N1 | 176.17 (5) | C8—C9—H9A | 121.0 |
| N2—Ni1—O6 | 77.83 (5) | C9—C10—C11 | 120.52 (14) |
| N1—Ni1—O6 | 104.64 (5) | C9—C10—H10A | 119.7 |
| N2—Ni1—O7 | 78.27 (5) | C11—C10—H10A | 119.7 |
| N1—Ni1—O7 | 99.37 (5) | C12—C11—C10 | 117.85 (14) |
| O6—Ni1—O7 | 155.96 (4) | C12—C11—H11A | 121.1 |
| N2—Ni1—O3 | 98.99 (5) | C10—C11—H11A | 121.1 |
| N1—Ni1—O3 | 77.94 (5) | N2—C12—C11 | 121.31 (14) |
| O6—Ni1—O3 | 95.64 (4) | N2—C12—C14 | 112.42 (14) |
| O7—Ni1—O3 | 90.55 (4) | C11—C12—C14 | 126.11 (13) |
| N2—Ni1—O2 | 105.48 (5) | O5—C13—O6 | 126.37 (14) |
| N1—Ni1—O2 | 77.70 (5) | O5—C13—C8 | 118.49 (13) |
| O6—Ni1—O2 | 87.29 (4) | O6—C13—C8 | 115.14 (12) |
| O7—Ni1—O2 | 96.66 (4) | O8—C14—O7 | 125.63 (14) |
| O3—Ni1—O2 | 155.41 (4) | O8—C14—C12 | 118.02 (13) |
| C6—O2—Ni1 | 114.09 (9) | O7—C14—C12 | 116.31 (12) |
| C7—O3—Ni1 | 114.43 (9) | C15—N3—H3B | 109.5 |
| C13—O6—Ni1 | 114.94 (9) | C15—N3—H3C | 109.5 |
| C14—O7—Ni1 | 113.70 (9) | H3B—N3—H3C | 109.5 |
| C5—N1—C1 | 121.44 (14) | C15—N3—H3D | 109.5 |
| C5—N1—Ni1 | 118.86 (10) | H3B—N3—H3D | 109.5 |
| C1—N1—Ni1 | 119.70 (10) | H3C—N3—H3D | 109.5 |
| C12—N2—C8 | 121.75 (15) | C16—N4—H4B | 109.5 |
| C12—N2—Ni1 | 118.82 (11) | C16—N4—H4C | 109.5 |
| C8—N2—Ni1 | 119.39 (11) | H4B—N4—H4C | 109.5 |
| N1—C1—C2 | 121.11 (14) | C16—N4—H4D | 109.5 |
| N1—C1—C6 | 112.38 (13) | H4B—N4—H4D | 109.5 |
| C2—C1—C6 | 126.50 (14) | H4C—N4—H4D | 109.5 |
| C1—C2—C3 | 117.99 (14) | N3—C15—C16 | 112.62 (12) |
| C1—C2—H2A | 121.0 | N3—C15—H15A | 109.1 |
| C3—C2—H2A | 121.0 | C16—C15—H15A | 109.1 |
| C4—C3—C2 | 120.40 (14) | N3—C15—H15B | 109.1 |
| C4—C3—H3A | 119.8 | C16—C15—H15B | 109.1 |
| C2—C3—H3A | 119.8 | H15A—C15—H15B | 107.8 |
| C5—C4—C3 | 117.93 (13) | N4—C16—C15 | 111.16 (11) |

| | | | |
|---|---|---|---|
| C5—C4—H4A | 121.0 | N4—C16—C17 | 109.06 (12) |
| C3—C4—H4A | 121.0 | C15—C16—C17 | 110.80 (12) |
| N1—C5—C4 | 121.13 (14) | N4—C16—H16A | 108.6 |
| N1—C5—C7 | 113.07 (13) | C15—C16—H16A | 108.6 |
| C4—C5—C7 | 125.70 (13) | C17—C16—H16A | 108.6 |
| O1—C6—O2 | 125.06 (13) | C16—C17—H17A | 109.5 |
| O1—C6—C1 | 118.90 (13) | C16—C17—H17B | 109.5 |
| O2—C6—C1 | 116.03 (12) | H17A—C17—H17B | 109.5 |
| O4—C7—O3 | 125.65 (13) | C16—C17—H17C | 109.5 |
| O4—C7—C5 | 118.88 (13) | H17A—C17—H17C | 109.5 |
| O3—C7—C5 | 115.46 (12) | H17B—C17—H17C | 109.5 |
| N2—C8—C9 | 120.62 (14) | H1WA—O1W—H1WB | 101.2 |
| N2—C8—C13 | 112.42 (13) | H2WA—O2W—H2WB | 104.5 |
| C9—C8—C13 | 126.95 (13) | H3WA—O3W—H3WB | 102.4 |
| C10—C9—C8 | 117.93 (14) | H4WA—O4W—H4WB | 89.5 |
| C10—C9—H9A | 121.0 | | |

| | | | |
|---|---|---|---|
| N2—Ni1—O2—C6 | 179.68 (10) | Ni1—N1—C5—C4 | −179.84 (10) |
| N1—Ni1—O2—C6 | −2.52 (10) | C1—N1—C5—C7 | 176.61 (12) |
| O6—Ni1—O2—C6 | 103.10 (10) | Ni1—N1—C5—C7 | −3.14 (16) |
| O7—Ni1—O2—C6 | −100.70 (10) | C3—C4—C5—N1 | 0.7 (2) |
| O3—Ni1—O2—C6 | 5.46 (16) | C3—C4—C5—C7 | −175.52 (13) |
| N2—Ni1—O3—C7 | 173.26 (10) | Ni1—O2—C6—O1 | −175.13 (11) |
| N1—Ni1—O3—C7 | −4.41 (10) | Ni1—O2—C6—C1 | 3.57 (15) |
| O6—Ni1—O3—C7 | −108.21 (10) | N1—C1—C6—O1 | 175.89 (13) |
| O7—Ni1—O3—C7 | 95.05 (10) | C2—C1—C6—O1 | −2.4 (2) |
| O2—Ni1—O3—C7 | −12.39 (16) | N1—C1—C6—O2 | −2.89 (18) |
| N2—Ni1—O6—C13 | −4.98 (10) | C2—C1—C6—O2 | 178.85 (14) |
| N1—Ni1—O6—C13 | 178.04 (10) | Ni1—O3—C7—O4 | −177.39 (11) |
| O7—Ni1—O6—C13 | 1.20 (16) | Ni1—O3—C7—C5 | 4.04 (15) |
| O3—Ni1—O6—C13 | −102.99 (10) | N1—C5—C7—O4 | −179.55 (13) |
| O2—Ni1—O6—C13 | 101.50 (10) | C4—C5—C7—O4 | −3.0 (2) |
| N2—Ni1—O7—C14 | −6.39 (10) | N1—C5—C7—O3 | −0.87 (18) |
| N1—Ni1—O7—C14 | 170.54 (10) | C4—C5—C7—O3 | 175.64 (13) |
| O6—Ni1—O7—C14 | −12.55 (15) | C12—N2—C8—C9 | −1.7 (2) |
| O3—Ni1—O7—C14 | 92.68 (10) | Ni1—N2—C8—C9 | 176.03 (11) |
| O2—Ni1—O7—C14 | −110.88 (10) | C12—N2—C8—C13 | 179.89 (12) |
| O6—Ni1—N1—C5 | 96.77 (11) | Ni1—N2—C8—C13 | −2.41 (16) |
| O7—Ni1—N1—C5 | −84.54 (11) | N2—C8—C9—C10 | 1.3 (2) |
| O3—Ni1—N1—C5 | 4.01 (11) | C13—C8—C9—C10 | 179.52 (14) |
| O2—Ni1—N1—C5 | −179.38 (12) | C8—C9—C10—C11 | 0.3 (2) |
| O6—Ni1—N1—C1 | −83.00 (12) | C9—C10—C11—C12 | −1.6 (2) |
| O7—Ni1—N1—C1 | 95.70 (11) | C8—N2—C12—C11 | 0.3 (2) |
| O3—Ni1—N1—C1 | −175.75 (12) | Ni1—N2—C12—C11 | −177.38 (10) |
| O2—Ni1—N1—C1 | 0.86 (11) | C8—N2—C12—C14 | 175.92 (12) |
| O6—Ni1—N2—C12 | −178.35 (11) | Ni1—N2—C12—C14 | −1.80 (16) |
| O7—Ni1—N2—C12 | 4.21 (10) | C10—C11—C12—N2 | 1.3 (2) |
| O3—Ni1—N2—C12 | −84.47 (11) | C10—C11—C12—C14 | −173.67 (13) |

| | | | |
|---|---|---|---|
| O2—Ni1—N2—C12 | 97.96 (11) | Ni1—O6—C13—O5 | −174.76 (11) |
| O6—Ni1—N2—C8 | 3.88 (10) | Ni1—O6—C13—C8 | 5.13 (15) |
| O7—Ni1—N2—C8 | −173.56 (11) | N2—C8—C13—O5 | 177.84 (12) |
| O3—Ni1—N2—C8 | 97.75 (11) | C9—C8—C13—O5 | −0.5 (2) |
| O2—Ni1—N2—C8 | −79.81 (11) | N2—C8—C13—O6 | −2.06 (18) |
| C5—N1—C1—C2 | −0.8 (2) | C9—C8—C13—O6 | 179.62 (14) |
| Ni1—N1—C1—C2 | 179.00 (11) | Ni1—O7—C14—O8 | −174.94 (12) |
| C5—N1—C1—C6 | −179.12 (12) | Ni1—O7—C14—C12 | 7.30 (15) |
| Ni1—N1—C1—C6 | 0.63 (16) | N2—C12—C14—O8 | 178.05 (12) |
| N1—C1—C2—C3 | 0.9 (2) | C11—C12—C14—O8 | −6.6 (2) |
| C6—C1—C2—C3 | 179.00 (13) | N2—C12—C14—O7 | −4.02 (18) |
| C1—C2—C3—C4 | −0.2 (2) | C11—C12—C14—O7 | 171.32 (14) |
| C2—C3—C4—C5 | −0.6 (2) | N3—C15—C16—N4 | −61.32 (15) |
| C1—N1—C5—C4 | −0.1 (2) | N3—C15—C16—C17 | 177.24 (12) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H1*WA*···O4*W* | 0.82 | 1.97 | 2.788 (2) | 173 |
| O1*W*—H1*WB*···O2 | 0.82 | 2.47 | 3.109 (2) | 135 |
| O1*W*—H1*WB*···O6 | 0.82 | 2.21 | 2.912 (2) | 144 |
| O2*W*—H2*WA*···O3 | 0.82 | 2.21 | 2.759 (2) | 125 |
| N3—H3*B*···O4$^{i}$ | 0.91 | 1.90 | 2.795 (2) | 168 |
| N3—H3*C*···O1*W* | 0.91 | 1.91 | 2.763 (2) | 155 |
| N3—H3*D*···O8$^{ii}$ | 0.91 | 1.88 | 2.783 (2) | 176 |
| O2*W*—H2*WB*···O1$^{iii}$ | 0.82 | 2.07 | 2.849 (2) | 160 |
| N4—H4*B*···O3*W*$^{ii}$ | 0.91 | 1.92 | 2.812 (2) | 165 |
| N4—H4*C*···O1 | 0.91 | 1.92 | 2.813 (2) | 168 |
| N4—H4*D*···O4*W*$^{iv}$ | 0.91 | 1.91 | 2.777 (2) | 160 |
| O3*W*—H3*WA*···O8 | 0.82 | 2.03 | 2.771 (2) | 149 |
| O3*W*—H3*WB*···O4$^{v}$ | 0.82 | 1.99 | 2.787 (2) | 166 |
| O4*W*—H4*WA*···O2*W*$^{i}$ | 0.82 | 1.99 | 2.749 (2) | 153 |
| O4*W*—H4*WB*···O5 | 0.82 | 1.90 | 2.712 (2) | 171 |
| C10—H10*A*···O6$^{vi}$ | 0.95 | 2.54 | 3.289 (2) | 136 |
| C11—H11*A*···O1*W*$^{vi}$ | 0.95 | 2.58 | 3.484 (2) | 160 |
| C15—H15*B*···O5$^{vii}$ | 0.99 | 2.30 | 3.268 (2) | 164 |
| C16—H16*A*···O7$^{ii}$ | 1.00 | 2.49 | 3.291 (2) | 137 |

Symmetry codes: (i) *x*+1/2, −*y*+3/2, *z*; (ii) *x*+1/2, −*y*+1/2, *z*; (iii) −*x*+1/2, *y*+1/2, *z*−1/2; (iv) *x*, *y*−1, *z*; (v) −*x*, −*y*+1, *z*−1/2; (vi) −*x*+1/2, *y*−1/2, *z*−1/2; (vii) −*x*+1, −*y*+1, *z*+1/2.