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

# Bis(guanidinium) bis(4-hydroxypyridine-2,6-dicarboxylato-$\kappa^3O^2,N,O^6$)nickelate(II) dihydrate

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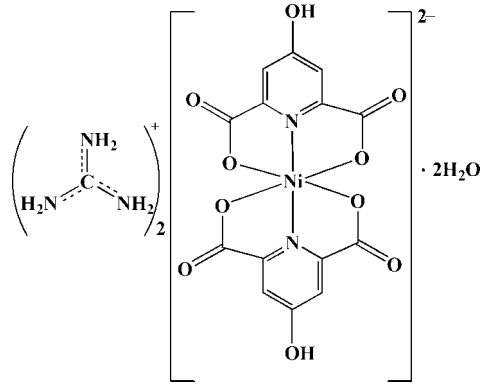
Received 5 November 2007; accepted 2 December 2007

Key indicators: single-crystal X-ray study; $T$ = 150 K; mean $\sigma$(C–C) = 0.001 Å; $R$ factor = 0.026; $wR$ factor = 0.076; data-to-parameter ratio = 31.4.

The reaction of nickel(II) nitrate hexahydrate, guanidine (G) and 4-hydroxypyridine-2,6-dicarboxylic acid ($hypydcH_2$) in a 1:2:2 molar ratio in aqueous solution resulted in the formation of the title compound, $(CH_6N_3)_2[Ni(C_7H_3NO_5)_2]\cdot 2H_2O$ or $(GH)_2[Ni(hypydc)_2]\cdot 2H_2O$. The six donor atoms of the two 4-hydroxypyridine-2,6-dicarboxylate or $(hypydc)^{2-}$ ligands form a distorted octahedral arrangement around the $Ni^{II}$ centre. Considerable C—O$\cdots\pi$ stacking interactions between the CO groups of carboxylate fragments and the pyridine rings of $(hypydc)^{2-}$ with a distance of 3.3212 (8) Å are observed. In the crystal structure, a wide range of noncovalent interactions consisting of hydrogen bonding (of the types O—H$\cdots$O and N—H$\cdots$O), ion pairing, and $\pi$–$\pi$ [centroid–centroid distance 3.8037 (5) Å], N—H$\cdots\pi$ and C—O$\cdots\pi$ stacking interactions connect the various components into a supramolecular structure.

## Related literature

For related literature, see: Aghabozorg, Attar Gharamaleki *et al.* (2007*a*, 2007*b*); Aghabozorg, Daneshvar *et al.* (2007).



## Experimental

### Crystal data

$(CH_6N_3)_2[Ni(C_7H_3NO_5)_2]\cdot 2H_2O$
$M_r$ = 577.13
Triclinic, $P\overline{1}$
$a$ = 8.9253 (6) Å
$b$ = 9.9060 (6) Å
$c$ = 13.2186 (9) Å
$\alpha$ = 101.415 (3)°
$\beta$ = 103.099 (3)°
$\gamma$ = 91.938 (3)°
$V$ = 1111.99 (13) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.96 mm$^{-1}$
$T$ = 150 (2) K
0.50 × 0.32 × 0.15 mm

### Data collection

Bruker SMART 1000 diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min}$ = 0.647, $T_{max}$ = 0.870
46516 measured reflections
10497 independent reflections
9650 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.019

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.076
$S$ = 1.06
10497 reflections
334 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.56 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.61 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Ni1—N2 | 1.9665 (6) | Ni1—O10 | 2.1387 (6) |
| Ni1—N1 | 1.9700 (6) | Ni1—O6 | 2.1477 (6) |
| Ni1—O1 | 2.1088 (6) | Ni1—O5 | 2.2149 (6) |
| N2—Ni1—N1 | 171.30 (3) | O1—Ni1—O10 | 93.41 (3) |
| O1—Ni1—O5 | 154.97 (2) | O6—Ni1—O5 | 91.30 (2) |
| O10—Ni1—O6 | 154.87 (2) | | |

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

*Cg*1 is the centroid of the N1/C2–C6 ring.

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O3—H3*C*$\cdots$O6$^{i}$ | 0.90 | 1.71 | 2.5901 (8) | 166 |
| O8—H8$\cdots$O5$^{ii}$ | 0.90 | 1.84 | 2.7057 (9) | 160 |
| O11—H11*A*$\cdots$O9$^{iii}$ | 0.90 | 1.86 | 2.7106 (9) | 156 |
| O11—H11*B*$\cdots$O2$^{iv}$ | 0.90 | 1.88 | 2.7464 (9) | 161 |
| O12—H12*B*$\cdots$O11$^{ii}$ | 0.90 | 2.15 | 3.0425 (12) | 172 |
| O12—H12*A*$\cdots$O5 | 0.90 | 2.15 | 3.0244 (13) | 164 |

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O12—H12$A$···O4 | 0.90 | 2.64 | 3.3823 (12) | 141 |
| N3—H3$A$···O4$^{v}$ | 0.90 | 2.15 | 2.9307 (10) | 144 |
| N3—H3$B$···O10 | 0.90 | 2.07 | 2.8817 (10) | 149 |
| N4—H4$A$···O4$^{v}$ | 0.90 | 1.97 | 2.8072 (11) | 154 |
| N4—H4$B$···O11$^{vi}$ | 0.90 | 2.06 | 2.9161 (10) | 159 |
| N5—H5$A$···O10 | 0.90 | 2.19 | 2.9887 (10) | 148 |
| N5—H5$B$···O2$^{vii}$ | 0.90 | 1.98 | 2.8656 (10) | 169 |
| N6—H6$A$···O7$^{viii}$ | 0.90 | 2.28 | 3.0178 (11) | 139 |
| N6—H6$A$···O1 | 0.90 | 2.49 | 3.0038 (9) | 117 |
| N6—H6$B$···O3$^{vii}$ | 0.90 | 2.55 | 3.2320 (11) | 133 |
| N7—H7$A$···O9$^{iii}$ | 0.90 | 2.01 | 2.8999 (10) | 172 |
| N7—H7$B$···O12$^{ix}$ | 0.90 | 1.93 | 2.8282 (13) | 176 |
| N8—H8$A$···O7$^{viii}$ | 0.90 | 1.94 | 2.7993 (10) | 158 |
| N8—H8$B$···O11 | 0.90 | 1.99 | 2.8847 (10) | 174 |
| N5—H5$A$···$Cg$1 | 0.90 | 3.47 | 3.362 (7) | 75 |

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $-x, -y, -z+1$; (v) $-x+1, -y+1, -z$; (vi) $x, y, z-1$; (vii) $-x, -y, -z$; (viii) $-x, -y+1, -z+1$; (ix) $x, y-1, z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2005) and *Mercury* (Version 1.4.2; Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Financial support from Ilam University and the Teacher Training University, Tehran, is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2189).

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# supporting information

*Acta Cryst.* (2008). E**64**, m144–m145 [https://doi.org/10.1107/S1600536807065026]

## Bis(guanidinium) bis(4-hydroxypyridine-2,6-dicarboxylato-$\kappa^3O^2,N,O^6$)nickelate(II) dihydrate

**Hossein Aghabozorg, Elham Motyeian, Jafar Attar Gharamaleki, Janet Soleimannejad, Mohammad Ghadermazi and Elizabeth Spey Sharon**

### S1. Comment

The non-covalent interactions such as ion pairing, hydrogen bonding and $\pi$–$\pi$ stacking are observed in these ionic compounds. The importance of weak hydrogen bonds in the context of crystal engineering, molecular recognition and supramolecular chemistry has been well recognized in recent years. 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-tetracarboxylicacid, $btcH_4$, to propane-1,3-diamine (pn) and 1,10-phenanthroline, (phen), resulted in the formation of novel self-assembled $(pnH_2)(pydc)\cdot(pydcH_2)\cdot 2.5H_2O$, $(pnH_2)_2(btc)\cdot 2H_2O$ and $(phenH)_4(btcH_3)_2(btcH_2)$ systems, respectively. The resulting compounds with some remaining sites as electron donors can coordinate to metallic ions (Aghabozorg, Attar Gharamaleki *et al.*, 2007*a*,b; Aghabozorg, Daneshvar *et al.*, 2007).

The molecular structure of the title compound is presented in Fig. 1. The $Ni^{II}$ atom is six-coordinated by two 4-hydroxy-pyridine-2,6-dicarboxylate, or $(hypydc)^{2-}$, groups, *i.e*. each $(hypydc)^{2-}$ is coordinated through one pyridine N atom and two carboxylate O atoms (Table 1). N1 and N2 atoms of the two $(hypydc)^{2-}$ fragments occupy the axial positions, while atoms O1, O5, O6 and O10 form the equatorial plane [with Ni—O distances ranging from 2.1088 (6) to 2.2150 (6) Å]. The N1—Ni1—N2 angle [171.30 (3)°] deviates from linearity. Therefore, the coordination around $Ni^{II}$ is distorted octahedral. The O5—Ni1—O6 and O1—Ni1—O10 angles are equal to 91.30 (2) and 93.41 (3)°, respectively. On the other hand, O1—Ni1—O6—C8 and O10—Ni1—O5—C7 torsion angles are 93.20 (5) and 92.27 (5) Å, respectively indicating that two $(hypydc)^{2-}$ units are almost perpendicular to each other.

A noticeable feature of the title compound is the presence of N—H···$\pi$ stacking interactions between N—H group of guanidinium ions with aromatic rings of $(hypydc)^{2-}$ units. The H···$\pi$ distance (measured to the centre of phenyl ring) is 3.475Å for N5—H5A···*Cg*1 [*Cg*1 is the centroid of N1/C2—C6 ring]. There is also $\pi$···$\pi$ stacking interaction betweentwo aromatic rings of $(hypydc)^{2-}$ units, with distance of 3.8037 (5) Å [-*x*, 1 - *y*, -*z*] (Fig. 2).

Also a considerable C—O···$\pi$ stacking interactions between CO groups of carboxylate fragments with aromatic rings of 4-hydroxypyridine-2,6-dicarboxylate with distances of 3.321 (8) Å for C8—O7···*Cg*2 (-*x*, 1 - *y*, 1 - *z*) [*Cg*2 is the centroid for N2/C9—C13 ring] are observed in the prepared compound (Fig. 3). In the crystal structure, a wide range of non-covalent interactions consisting of hydrogen bonding (of the type of O—H···O and N—H···O with D···A ranging from 2.5901 (8) Å to 3.3823 (12) Å), ion pairing, $\pi$···$\pi$, N—H···$\pi$ and C—O···$\pi$ stacking connect the various components into a supramolecular structure (Table 2, Figs. 4 and 5).

## S2. Experimental

An aqueous solution of sodium hydroxide (80 mg, 2 mmol) was added to guanidine hydrochloride (200 mg, 2 mmol) in a 1:1 molar ratio. The resulting suspension was stirred for 1 h and filtered. An aqueous solution of $Ni(NO_3)_2.6H_2O$ (290 mg, 1 mmol) and 4-hydroxypyridine-2,6-dicarboxylic (360 mg, 2 mmol) acid was added to the filtered solution in a 1:2 molar ratio, and the reaction mixture was heated to boiling point for 2 h. Green crystals were obtained from the solution after two days at room temperature.

## S3. Refinement

Hydrogen atoms were positioned geometrically and refined with a riding model with O—H = 0.95 Å, and with U(H) constrained to be 1.2 times U~eq~ of the carrier atom.

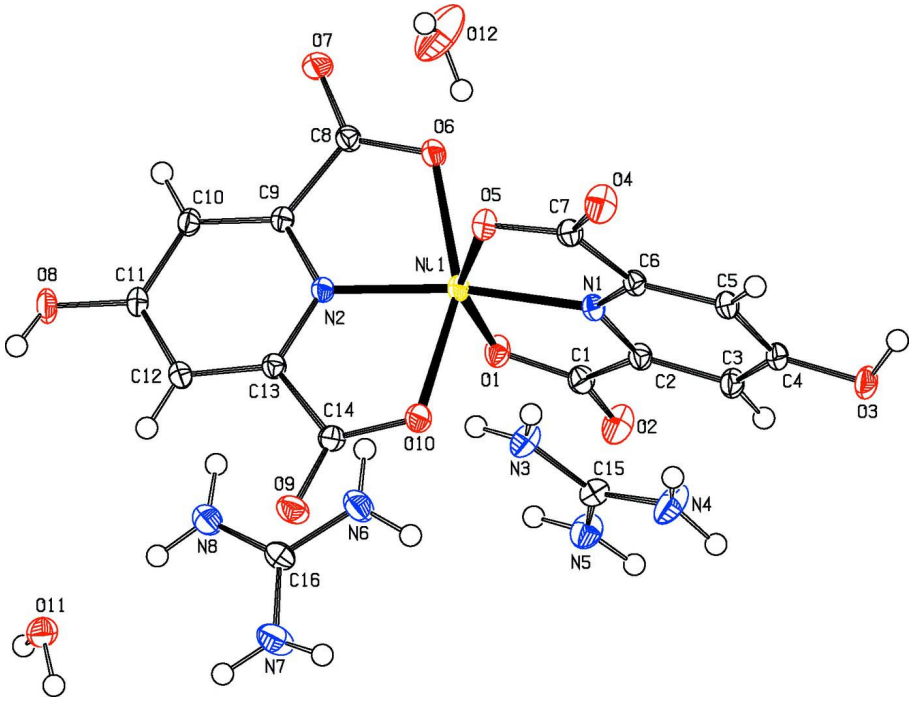


**Figure 1**

The structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

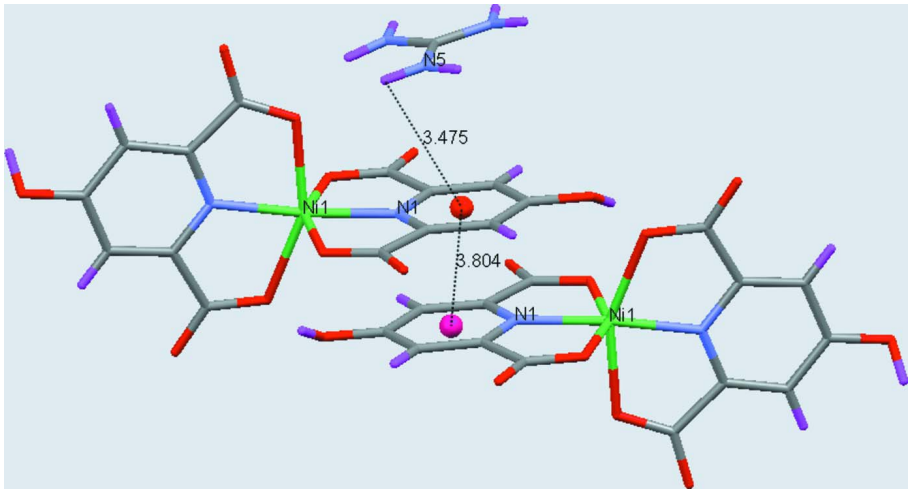


**Figure 2**

$\pi\cdots\pi$ Stacking interaction between two aromatic rings of $(hypydc)^{2-}$ units, with distance of 3.8037 (5) Å [-*x*, 1 - *y*, -*z*]; N—H$\cdots\pi$ stacking interaction between N—H groups of guanidinium ions with aromatic rings of $(hypydc)^{2-}$ units. The H$\cdots\pi$ distance (measured to the centre of phenyl ring) is 2.96 Å for N5—H5A$\cdots$*Cg*1 [*Cg*1 is the centroid of N1/C2—C6 ring].

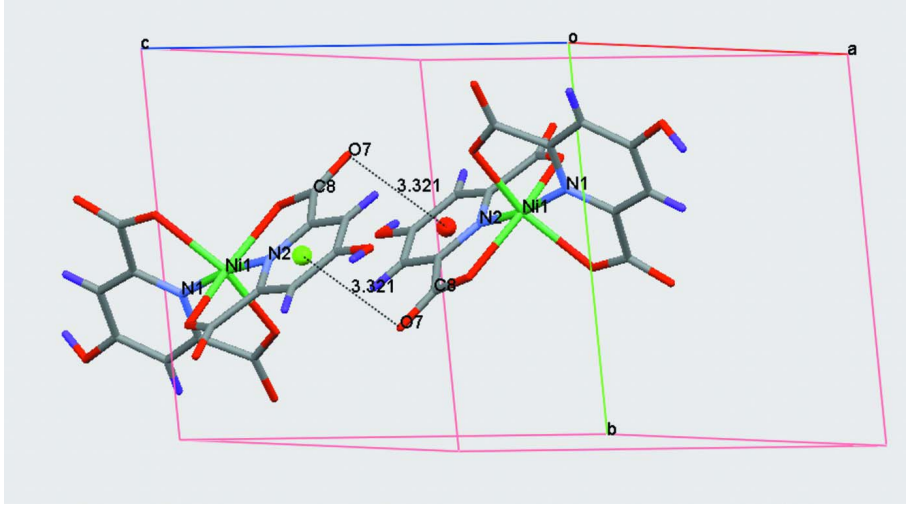


**Figure 3**

C—O$\cdots\pi$ stacking interactions between CO groups of carboxylate fragments with aromatic rings of 4-hydroxy-pyridine-2,6-dicarboxylate with distances of 3.321 (8) Å for C8—O7$\cdots$*Cg*2 (-*x*, 1 - *y*, 1 - *z*) [*Cg*2 is the centroid for N2/C9—C13 ring].

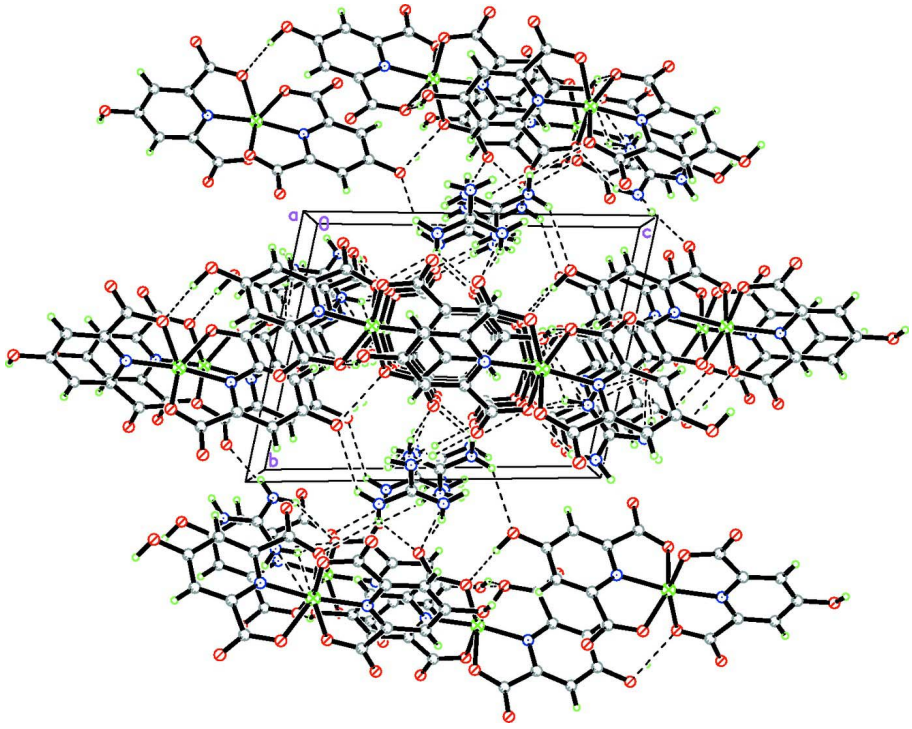

**Figure 4**

A layered packing diagram. The space between the two layers of $[Ni(hypydc)_2]^{2-}$ fragments is filled with a layer of $(GH)^+$ cations and water molecules.

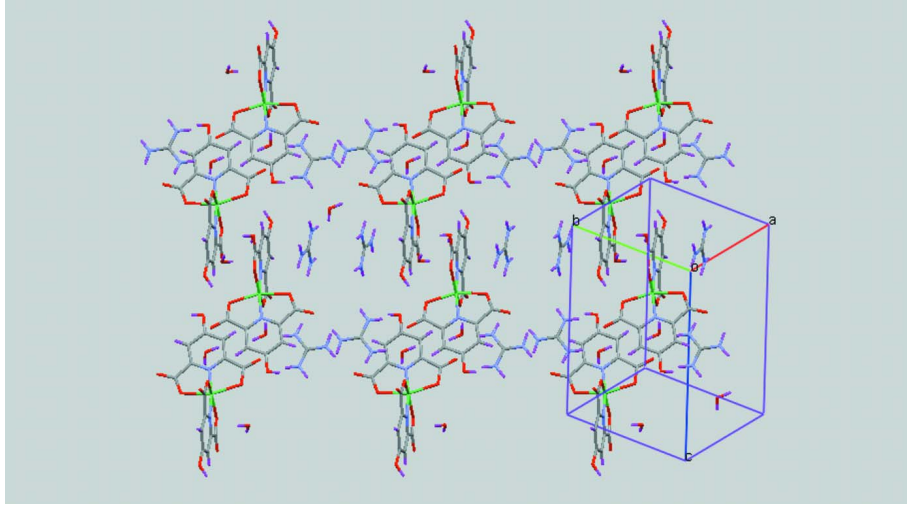

**Figure 5**

The crystal packing of the title compound view down the *a* axis; hydrogen bonds are shown as dashed lines.

**Bis(guanidinium) bis(4-hydroxypyridine-2,6-dicarboxylato-$\kappa^3O^2,N,O^6$)nickelate(II) dihydrate**

*Crystal data*

$(CH_6N_3)_2[Ni(C_7H_3NO_5)_2]\cdot 2H_2O$
$M_r = 577.13$
Triclinic, $P\overline{1}$

$a = 8.9253\ (6)$ Å
$b = 9.9060\ (6)$ Å
$c = 13.2186\ (9)$ Å

$\alpha$ = 101.415 (3)°
$\beta$ = 103.099 (3)°
$\gamma$ = 91.938 (3)°
$V$ = 1111.99 (13) Å$^3$
$Z$ = 2
$F$(000) = 596
$D_x$ = 1.724 Mg m$^{-3}$

Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9699 reflections
$\theta$ = 2.4–36.3°
$\mu$ = 0.96 mm$^{-1}$
$T$ = 150 K
Block, green
0.50 × 0.32 × 0.15 mm

*Data collection*

Bruker SMART 1000 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min}$ = 0.647, $T_{max}$ = 0.870

46516 measured reflections
10497 independent reflections
9650 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.019
$\theta_{max}$ = 36.4°, $\theta_{min}$ = 1.6°
$h$ = −14→11
$k$ = −16→16
$l$ = −21→21

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.076
$S$ = 1.06
10497 reflections
334 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.2702P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.56 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.61 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 | 0.173117 (11) | 0.423258 (10) | 0.259400 (7) | 0.01287 (3) |
| O1 | −0.00784 (7) | 0.27245 (6) | 0.24384 (5) | 0.01774 (10) |
| O2 | −0.16765 (9) | 0.11004 (7) | 0.12138 (5) | 0.02439 (13) |
| O3 | −0.02586 (9) | 0.20971 (7) | −0.21698 (5) | 0.02167 (12) |
| H3C | −0.0206 | 0.2745 | −0.2554 | 0.026* |
| O4 | 0.35691 (8) | 0.60277 (7) | 0.04763 (5) | 0.02381 (12) |
| O5 | 0.31707 (7) | 0.56247 (6) | 0.20082 (5) | 0.01687 (10) |
| O6 | 0.05225 (7) | 0.59263 (6) | 0.32052 (4) | 0.01635 (10) |
| O7 | 0.02582 (8) | 0.72029 (7) | 0.47531 (5) | 0.02065 (11) |

| | | | | |
|---|---|---|---|---|
| O8 | 0.37838 (8) | 0.46857 (7) | 0.73456 (5) | 0.02054 (11) |
| H8 | 0.4719 | 0.4367 | 0.7525 | 0.025* |
| O9 | 0.51375 (8) | 0.19318 (7) | 0.39007 (5) | 0.02143 (11) |
| O10 | 0.34554 (7) | 0.27853 (6) | 0.26981 (5) | 0.01768 (10) |
| O11 | 0.32536 (8) | −0.04310 (7) | 0.73709 (5) | 0.02032 (11) |
| H11A | 0.3814 | −0.1076 | 0.7089 | 0.024* |
| H11B | 0.2653 | −0.0814 | 0.7719 | 0.024* |
| O12 | 0.37899 (13) | 0.87354 (12) | 0.25296 (8) | 0.0491 (3) |
| H12B | 0.4704 | 0.9157 | 0.2539 | 0.059* |
| H12A | 0.3664 | 0.7820 | 0.2257 | 0.059* |
| N1 | 0.09970 (7) | 0.36856 (6) | 0.10372 (5) | 0.01309 (10) |
| N2 | 0.25270 (7) | 0.44832 (6) | 0.41390 (5) | 0.01274 (10) |
| N3 | 0.50285 (9) | 0.28895 (8) | 0.10335 (6) | 0.02072 (13) |
| H3A | 0.5659 | 0.3475 | 0.0847 | 0.025* |
| H3B | 0.4860 | 0.3064 | 0.1691 | 0.025* |
| N4 | 0.43549 (11) | 0.16824 (9) | −0.06920 (7) | 0.02808 (17) |
| H4A | 0.5014 | 0.2288 | −0.0833 | 0.034* |
| H4B | 0.3907 | 0.0927 | −0.1182 | 0.034* |
| N5 | 0.32885 (10) | 0.09767 (8) | 0.05716 (6) | 0.02313 (14) |
| H5A | 0.3226 | 0.1189 | 0.1254 | 0.028* |
| H5B | 0.2719 | 0.0285 | 0.0071 | 0.028* |
| N6 | 0.12908 (10) | 0.08178 (8) | 0.38427 (6) | 0.02258 (13) |
| H6A | 0.0636 | 0.1481 | 0.3920 | 0.027* |
| H6B | 0.1274 | 0.0351 | 0.3182 | 0.027* |
| N7 | 0.29526 (10) | −0.06930 (9) | 0.45012 (7) | 0.02577 (15) |
| H7A | 0.3483 | −0.1044 | 0.5041 | 0.031* |
| H7B | 0.3174 | −0.0873 | 0.3859 | 0.031* |
| N8 | 0.18342 (10) | 0.08088 (8) | 0.56283 (6) | 0.02222 (13) |
| H8A | 0.1141 | 0.1442 | 0.5680 | 0.027* |
| H8B | 0.2214 | 0.0388 | 0.6166 | 0.027* |
| C1 | −0.06666 (9) | 0.20926 (8) | 0.14912 (6) | 0.01563 (12) |
| C2 | −0.00601 (8) | 0.26094 (7) | 0.06391 (6) | 0.01391 (11) |
| C3 | −0.04990 (9) | 0.20506 (8) | −0.04397 (6) | 0.01656 (12) |
| H3 | −0.1226 | 0.1295 | −0.0705 | 0.020* |
| C4 | 0.01756 (9) | 0.26469 (8) | −0.11267 (6) | 0.01546 (12) |
| C5 | 0.12882 (9) | 0.37751 (8) | −0.06979 (6) | 0.01465 (11) |
| H5 | 0.1754 | 0.4190 | −0.1134 | 0.018* |
| C6 | 0.16685 (8) | 0.42490 (7) | 0.03947 (5) | 0.01292 (11) |
| C7 | 0.28988 (9) | 0.53963 (8) | 0.09859 (6) | 0.01487 (11) |
| C8 | 0.08025 (9) | 0.62575 (7) | 0.42266 (6) | 0.01421 (11) |
| C9 | 0.19209 (8) | 0.53834 (7) | 0.47982 (5) | 0.01287 (11) |
| C10 | 0.23152 (9) | 0.54827 (8) | 0.58878 (6) | 0.01447 (11) |
| H10 | 0.1879 | 0.6108 | 0.6338 | 0.017* |
| C11 | 0.33960 (9) | 0.46069 (8) | 0.62872 (6) | 0.01443 (11) |
| C12 | 0.40380 (9) | 0.36772 (8) | 0.55896 (6) | 0.01472 (11) |
| H12 | 0.4767 | 0.3100 | 0.5843 | 0.018* |
| C13 | 0.35558 (8) | 0.36443 (7) | 0.45134 (6) | 0.01300 (11) |
| C14 | 0.41057 (9) | 0.26960 (7) | 0.36476 (6) | 0.01460 (11) |

| | | | | |
|---|---|---|---|---|
| C15 | 0.42237 (9) | 0.18398 (8) | 0.03028 (6) | 0.01729 (12) |
| C16 | 0.20223 (9) | 0.02991 (8) | 0.46651 (7) | 0.01741 (12) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.01507 (5) | 0.01471 (4) | 0.00908 (4) | 0.00167 (3) | 0.00287 (3) | 0.00302 (3) |
| O1 | 0.0216 (3) | 0.0205 (2) | 0.0116 (2) | −0.0011 (2) | 0.00473 (19) | 0.00417 (18) |
| O2 | 0.0293 (3) | 0.0251 (3) | 0.0181 (3) | −0.0102 (2) | 0.0079 (2) | 0.0024 (2) |
| O3 | 0.0347 (3) | 0.0192 (2) | 0.0091 (2) | −0.0019 (2) | 0.0017 (2) | 0.00284 (18) |
| O4 | 0.0263 (3) | 0.0261 (3) | 0.0201 (3) | −0.0075 (2) | 0.0076 (2) | 0.0064 (2) |
| O5 | 0.0173 (2) | 0.0194 (2) | 0.0125 (2) | −0.00028 (18) | 0.00219 (18) | 0.00193 (18) |
| O6 | 0.0193 (2) | 0.0184 (2) | 0.0119 (2) | 0.00462 (19) | 0.00323 (18) | 0.00461 (18) |
| O7 | 0.0252 (3) | 0.0201 (3) | 0.0179 (2) | 0.0094 (2) | 0.0069 (2) | 0.0034 (2) |
| O8 | 0.0218 (3) | 0.0283 (3) | 0.0092 (2) | 0.0049 (2) | −0.00023 (19) | 0.0026 (2) |
| O9 | 0.0243 (3) | 0.0229 (3) | 0.0208 (3) | 0.0117 (2) | 0.0086 (2) | 0.0079 (2) |
| O10 | 0.0230 (3) | 0.0196 (2) | 0.0121 (2) | 0.0061 (2) | 0.00636 (19) | 0.00398 (18) |
| O11 | 0.0262 (3) | 0.0188 (2) | 0.0177 (2) | 0.0029 (2) | 0.0082 (2) | 0.0044 (2) |
| O12 | 0.0487 (5) | 0.0521 (6) | 0.0417 (5) | −0.0196 (5) | 0.0255 (4) | −0.0149 (4) |
| N1 | 0.0141 (2) | 0.0150 (2) | 0.0107 (2) | 0.00126 (19) | 0.00302 (18) | 0.00398 (18) |
| N2 | 0.0140 (2) | 0.0139 (2) | 0.0106 (2) | 0.00212 (18) | 0.00304 (18) | 0.00285 (18) |
| N3 | 0.0222 (3) | 0.0198 (3) | 0.0177 (3) | −0.0040 (2) | 0.0059 (2) | −0.0021 (2) |
| N4 | 0.0392 (4) | 0.0245 (3) | 0.0186 (3) | −0.0094 (3) | 0.0127 (3) | −0.0046 (3) |
| N5 | 0.0268 (3) | 0.0208 (3) | 0.0212 (3) | −0.0058 (3) | 0.0068 (3) | 0.0031 (2) |
| N6 | 0.0266 (3) | 0.0242 (3) | 0.0192 (3) | 0.0068 (3) | 0.0045 (3) | 0.0103 (3) |
| N7 | 0.0300 (4) | 0.0283 (4) | 0.0263 (4) | 0.0142 (3) | 0.0130 (3) | 0.0135 (3) |
| N8 | 0.0262 (3) | 0.0229 (3) | 0.0187 (3) | 0.0076 (3) | 0.0047 (3) | 0.0068 (2) |
| C1 | 0.0180 (3) | 0.0167 (3) | 0.0136 (3) | 0.0009 (2) | 0.0053 (2) | 0.0047 (2) |
| C2 | 0.0154 (3) | 0.0152 (3) | 0.0115 (3) | 0.0008 (2) | 0.0029 (2) | 0.0041 (2) |
| C3 | 0.0202 (3) | 0.0167 (3) | 0.0118 (3) | −0.0015 (2) | 0.0020 (2) | 0.0035 (2) |
| C4 | 0.0205 (3) | 0.0156 (3) | 0.0098 (2) | 0.0018 (2) | 0.0020 (2) | 0.0034 (2) |
| C5 | 0.0179 (3) | 0.0161 (3) | 0.0109 (2) | 0.0018 (2) | 0.0038 (2) | 0.0046 (2) |
| C6 | 0.0137 (3) | 0.0148 (3) | 0.0109 (2) | 0.0017 (2) | 0.0030 (2) | 0.0041 (2) |
| C7 | 0.0148 (3) | 0.0157 (3) | 0.0144 (3) | 0.0010 (2) | 0.0036 (2) | 0.0036 (2) |
| C8 | 0.0150 (3) | 0.0149 (3) | 0.0135 (3) | 0.0021 (2) | 0.0036 (2) | 0.0043 (2) |
| C9 | 0.0140 (3) | 0.0136 (2) | 0.0109 (2) | 0.0013 (2) | 0.0028 (2) | 0.0023 (2) |
| C10 | 0.0159 (3) | 0.0160 (3) | 0.0106 (2) | 0.0012 (2) | 0.0024 (2) | 0.0016 (2) |
| C11 | 0.0151 (3) | 0.0171 (3) | 0.0098 (2) | −0.0002 (2) | 0.0010 (2) | 0.0023 (2) |
| C12 | 0.0154 (3) | 0.0163 (3) | 0.0122 (3) | 0.0022 (2) | 0.0016 (2) | 0.0040 (2) |
| C13 | 0.0140 (3) | 0.0137 (3) | 0.0117 (2) | 0.0017 (2) | 0.0033 (2) | 0.0032 (2) |
| C14 | 0.0168 (3) | 0.0146 (3) | 0.0140 (3) | 0.0027 (2) | 0.0059 (2) | 0.0039 (2) |
| C15 | 0.0180 (3) | 0.0152 (3) | 0.0180 (3) | 0.0007 (2) | 0.0051 (2) | 0.0011 (2) |
| C16 | 0.0171 (3) | 0.0176 (3) | 0.0197 (3) | 0.0023 (2) | 0.0051 (2) | 0.0082 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ni1—N2 | 1.9665 (6) | N4—H4A | 0.9000 |
| Ni1—N1 | 1.9700 (6) | N4—H4B | 0.9000 |

| | | | |
|---|---|---|---|
| Ni1—O1 | 2.1088 (6) | N5—C15 | 1.3267 (11) |
| Ni1—O10 | 2.1387 (6) | N5—H5A | 0.9002 |
| Ni1—O6 | 2.1477 (6) | N5—H5B | 0.9000 |
| Ni1—O5 | 2.2149 (6) | N6—C16 | 1.3394 (10) |
| O1—C1 | 1.2668 (9) | N6—H6A | 0.9000 |
| O2—C1 | 1.2492 (10) | N6—H6B | 0.9001 |
| O3—C4 | 1.3394 (9) | N7—C16 | 1.3247 (11) |
| O3—H3C | 0.9000 | N7—H7A | 0.9000 |
| O4—C7 | 1.2357 (9) | N7—H7B | 0.8999 |
| O5—C7 | 1.2895 (9) | N8—C16 | 1.3238 (11) |
| O6—C8 | 1.2880 (9) | N8—H8A | 0.9000 |
| O7—C8 | 1.2343 (10) | N8—H8B | 0.9002 |
| O8—C11 | 1.3485 (9) | C1—C2 | 1.5198 (10) |
| O8—H8 | 0.9000 | C2—C3 | 1.3832 (10) |
| O9—C14 | 1.2413 (9) | C3—C4 | 1.4044 (11) |
| O10—C14 | 1.2796 (9) | C3—H3 | 0.9300 |
| O11—H11A | 0.9000 | C4—C5 | 1.4055 (11) |
| O11—H11B | 0.9001 | C5—C6 | 1.3857 (10) |
| O12—H12B | 0.9000 | C5—H5 | 0.9300 |
| O12—H12A | 0.9000 | C6—C7 | 1.5111 (10) |
| N1—C6 | 1.3371 (9) | C8—C9 | 1.5141 (10) |
| N1—C2 | 1.3374 (9) | C9—C10 | 1.3856 (10) |
| N2—C9 | 1.3363 (9) | C10—C11 | 1.4032 (11) |
| N2—C13 | 1.3368 (9) | C10—H10 | 0.9300 |
| N3—C15 | 1.3296 (10) | C11—C12 | 1.4021 (11) |
| N3—H3A | 0.9001 | C12—C13 | 1.3833 (10) |
| N3—H3B | 0.9001 | C12—H12 | 0.9300 |
| N4—C15 | 1.3256 (11) | C13—C14 | 1.5143 (10) |

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|---|---|---|---|
| N2—Ni1—N1 | 171.30 (3) | O2—C1—C2 | 118.69 (7) |
| O1—Ni1—O5 | 154.97 (2) | O1—C1—C2 | 115.64 (6) |
| O10—Ni1—O6 | 154.87 (2) | N1—C2—C3 | 121.56 (7) |
| N2—Ni1—O1 | 96.84 (2) | N1—C2—C1 | 112.83 (6) |
| N1—Ni1—O1 | 78.70 (2) | C3—C2—C1 | 125.60 (7) |
| N2—Ni1—O10 | 77.95 (2) | C2—C3—C4 | 118.69 (7) |
| N1—Ni1—O10 | 94.76 (2) | C2—C3—H3 | 120.7 |
| O1—Ni1—O10 | 93.41 (3) | C4—C3—H3 | 120.7 |
| N2—Ni1—O6 | 77.41 (2) | O3—C4—C3 | 118.15 (7) |
| N1—Ni1—O6 | 110.20 (2) | O3—C4—C5 | 122.66 (7) |
| O1—Ni1—O6 | 94.31 (2) | C3—C4—C5 | 119.18 (7) |
| N2—Ni1—O5 | 108.19 (2) | C6—C5—C4 | 117.89 (6) |
| N1—Ni1—O5 | 76.46 (2) | C6—C5—H5 | 121.1 |
| O10—Ni1—O5 | 91.73 (2) | C4—C5—H5 | 121.1 |
| O6—Ni1—O5 | 91.30 (2) | N1—C6—C5 | 122.25 (7) |
| C1—O1—Ni1 | 114.35 (5) | N1—C6—C7 | 113.16 (6) |
| C4—O3—H3C | 111.0 | C5—C6—C7 | 124.55 (6) |
| C7—O5—Ni1 | 113.28 (5) | O4—C7—O5 | 125.12 (7) |
| C8—O6—Ni1 | 114.63 (5) | O4—C7—C6 | 119.22 (7) |

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|---|---|---|---|
| C11—O8—H8 | 109.2 | O5—C7—C6 | 115.66 (6) |
| C14—O10—Ni1 | 114.35 (5) | O7—C8—O6 | 126.10 (7) |
| H11A—O11—H11B | 109.4 | O7—C8—C9 | 119.17 (7) |
| H12B—O12—H12A | 115.5 | O6—C8—C9 | 114.73 (6) |
| C6—N1—C2 | 120.41 (6) | N2—C9—C10 | 121.93 (7) |
| C6—N1—Ni1 | 121.23 (5) | N2—C9—C8 | 112.93 (6) |
| C2—N1—Ni1 | 117.81 (5) | C10—C9—C8 | 125.14 (7) |
| C9—N2—C13 | 120.78 (6) | C9—C10—C11 | 117.64 (7) |
| C9—N2—Ni1 | 119.82 (5) | C9—C10—H10 | 121.2 |
| C13—N2—Ni1 | 119.03 (5) | C11—C10—H10 | 121.2 |
| C15—N3—H3A | 119.6 | O8—C11—C12 | 121.73 (7) |
| C15—N3—H3B | 119.6 | O8—C11—C10 | 118.30 (7) |
| H3A—N3—H3B | 120.4 | C12—C11—C10 | 119.96 (6) |
| C15—N4—H4A | 117.6 | C13—C12—C11 | 118.05 (7) |
| C15—N4—H4B | 120.5 | C13—C12—H12 | 121.0 |
| H4A—N4—H4B | 121.3 | C11—C12—H12 | 121.0 |
| C15—N5—H5A | 115.0 | N2—C13—C12 | 121.62 (7) |
| C15—N5—H5B | 119.8 | N2—C13—C14 | 113.12 (6) |
| H5A—N5—H5B | 125.0 | C12—C13—C14 | 125.25 (7) |
| C16—N6—H6A | 121.8 | O9—C14—O10 | 125.71 (7) |
| C16—N6—H6B | 118.1 | O9—C14—C13 | 119.11 (7) |
| H6A—N6—H6B | 118.4 | O10—C14—C13 | 115.17 (6) |
| C16—N7—H7A | 121.3 | N4—C15—N5 | 120.87 (8) |
| C16—N7—H7B | 116.5 | N4—C15—N3 | 119.19 (8) |
| H7A—N7—H7B | 121.1 | N5—C15—N3 | 119.93 (8) |
| C16—N8—H8A | 116.9 | N8—C16—N7 | 121.25 (8) |
| C16—N8—H8B | 119.8 | N8—C16—N6 | 119.57 (8) |
| H8A—N8—H8B | 121.8 | N7—C16—N6 | 119.16 (8) |
| O2—C1—O1 | 125.67 (7) | | |

| | | | |
|---|---|---|---|
| N2—Ni1—O1—C1 | −165.80 (6) | O2—C1—C2—C3 | −1.87 (12) |
| N1—Ni1—O1—C1 | 6.63 (6) | O1—C1—C2—C3 | 177.90 (8) |
| O10—Ni1—O1—C1 | −87.54 (6) | N1—C2—C3—C4 | −0.79 (12) |
| O6—Ni1—O1—C1 | 116.39 (6) | C1—C2—C3—C4 | −179.78 (7) |
| O5—Ni1—O1—C1 | 13.95 (10) | C2—C3—C4—O3 | −179.99 (7) |
| N2—Ni1—O5—C7 | 170.16 (5) | C2—C3—C4—C5 | 0.95 (12) |
| N1—Ni1—O5—C7 | −2.20 (5) | O3—C4—C5—C6 | −179.04 (7) |
| O1—Ni1—O5—C7 | −9.58 (9) | C3—C4—C5—C6 | −0.02 (11) |
| O10—Ni1—O5—C7 | 92.27 (5) | C2—N1—C6—C5 | 1.36 (11) |
| O6—Ni1—O5—C7 | −112.67 (5) | Ni1—N1—C6—C5 | 172.68 (5) |
| N2—Ni1—O6—C8 | −2.86 (5) | C2—N1—C6—C7 | −176.55 (6) |
| N1—Ni1—O6—C8 | 172.73 (5) | Ni1—N1—C6—C7 | −5.23 (8) |
| O1—Ni1—O6—C8 | 93.20 (5) | C4—C5—C6—N1 | −1.14 (11) |
| O10—Ni1—O6—C8 | −14.34 (9) | C4—C5—C6—C7 | 176.52 (7) |
| O5—Ni1—O6—C8 | −111.22 (5) | Ni1—O5—C7—O4 | −179.06 (7) |
| N2—Ni1—O10—C14 | 3.50 (5) | Ni1—O5—C7—C6 | 0.27 (8) |
| N1—Ni1—O10—C14 | −171.70 (6) | N1—C6—C7—O4 | −177.72 (7) |
| O1—Ni1—O10—C14 | −92.77 (6) | C5—C6—C7—O4 | 4.43 (12) |

| | | | |
|---|---|---|---|
| O6—Ni1—O10—C14 | 14.95 (9) | N1—C6—C7—O5 | 2.91 (10) |
| O5—Ni1—O10—C14 | 111.74 (6) | C5—C6—C7—O5 | −174.94 (7) |
| N2—Ni1—N1—C6 | −119.19 (16) | Ni1—O6—C8—O7 | 179.06 (7) |
| O1—Ni1—N1—C6 | −179.02 (6) | Ni1—O6—C8—C9 | −0.37 (8) |
| O10—Ni1—N1—C6 | −86.48 (6) | C13—N2—C9—C10 | −0.51 (11) |
| O6—Ni1—N1—C6 | 90.51 (6) | Ni1—N2—C9—C10 | 172.42 (5) |
| O5—Ni1—N1—C6 | 4.16 (6) | C13—N2—C9—C8 | 178.98 (6) |
| N2—Ni1—N1—C2 | 52.35 (19) | Ni1—N2—C9—C8 | −8.09 (8) |
| O1—Ni1—N1—C2 | −7.48 (6) | O7—C8—C9—N2 | −174.29 (7) |
| O10—Ni1—N1—C2 | 85.06 (6) | O6—C8—C9—N2 | 5.18 (9) |
| O6—Ni1—N1—C2 | −97.95 (6) | O7—C8—C9—C10 | 5.17 (11) |
| O5—Ni1—N1—C2 | 175.70 (6) | O6—C8—C9—C10 | −175.36 (7) |
| N1—Ni1—N2—C9 | −145.37 (15) | N2—C9—C10—C11 | 0.58 (11) |
| O1—Ni1—N2—C9 | −86.74 (6) | C8—C9—C10—C11 | −178.84 (7) |
| O10—Ni1—N2—C9 | −178.78 (6) | C9—C10—C11—O8 | −179.59 (7) |
| O6—Ni1—N2—C9 | 6.18 (5) | C9—C10—C11—C12 | 0.16 (11) |
| O5—Ni1—N2—C9 | 93.38 (6) | O8—C11—C12—C13 | 178.81 (7) |
| N1—Ni1—N2—C13 | 27.7 (2) | C10—C11—C12—C13 | −0.94 (11) |
| O1—Ni1—N2—C13 | 86.32 (6) | C9—N2—C13—C12 | −0.33 (11) |
| O10—Ni1—N2—C13 | −5.72 (5) | Ni1—N2—C13—C12 | −173.32 (5) |
| O6—Ni1—N2—C13 | 179.23 (6) | C9—N2—C13—C14 | 179.79 (6) |
| O5—Ni1—N2—C13 | −93.57 (6) | Ni1—N2—C13—C14 | 6.80 (8) |
| Ni1—O1—C1—O2 | 174.96 (7) | C11—C12—C13—N2 | 1.04 (11) |
| Ni1—O1—C1—C2 | −4.79 (9) | C11—C12—C13—C14 | −179.09 (7) |
| C6—N1—C2—C3 | −0.36 (11) | Ni1—O10—C14—O9 | −179.76 (7) |
| Ni1—N1—C2—C3 | −171.97 (6) | Ni1—O10—C14—C13 | −1.05 (8) |
| C6—N1—C2—C1 | 178.76 (6) | N2—C13—C14—O9 | 175.34 (7) |
| Ni1—N1—C2—C1 | 7.15 (8) | C12—C13—C14—O9 | −4.54 (11) |
| O2—C1—C2—N1 | 179.06 (7) | N2—C13—C14—O10 | −3.46 (9) |
| O1—C1—C2—N1 | −1.17 (10) | C12—C13—C14—O10 | 176.66 (7) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3*C*···O6$^{i}$ | 0.90 | 1.71 | 2.5901 (8) | 166 |
| O8—H8···O5$^{ii}$ | 0.90 | 1.84 | 2.7057 (9) | 160 |
| O11—H11*A*···O9$^{iii}$ | 0.90 | 1.86 | 2.7106 (9) | 156 |
| O11—H11*B*···O2$^{iv}$ | 0.90 | 1.88 | 2.7464 (9) | 161 |
| O12—H12*B*···O11$^{ii}$ | 0.90 | 2.15 | 3.0425 (12) | 172 |
| O12—H12*A*···O5 | 0.90 | 2.15 | 3.0244 (13) | 164 |
| O12—H12*A*···O4 | 0.90 | 2.64 | 3.3823 (12) | 141 |
| N3—H3*A*···O4$^{v}$ | 0.90 | 2.15 | 2.9307 (10) | 144 |
| N3—H3*B*···O10 | 0.90 | 2.07 | 2.8817 (10) | 149 |
| N4—H4*A*···O4$^{v}$ | 0.90 | 1.97 | 2.8072 (11) | 154 |
| N4—H4*B*···O11$^{vi}$ | 0.90 | 2.06 | 2.9161 (10) | 159 |
| N5—H5*A*···O10 | 0.90 | 2.19 | 2.9887 (10) | 148 |
| N5—H5*B*···O2$^{vii}$ | 0.90 | 1.98 | 2.8656 (10) | 169 |
| N6—H6*A*···O7$^{viii}$ | 0.90 | 2.28 | 3.0178 (11) | 139 |

| | | | | |
|---|---|---|---|---|
| N6—H6*A*···O1 | 0.90 | 2.49 | 3.0038 (9) | 117 |
| N6—H6*B*···O3$^{vii}$ | 0.90 | 2.55 | 3.2320 (11) | 133 |
| N7—H7*A*···O9$^{iii}$ | 0.90 | 2.01 | 2.8999 (10) | 172 |
| N7—H7*B*···O12$^{ix}$ | 0.90 | 1.93 | 2.8282 (13) | 176 |
| N8—H8*A*···O7$^{viii}$ | 0.90 | 1.94 | 2.7993 (10) | 158 |
| N8—H8*B*···O11 | 0.90 | 1.99 | 2.8847 (10) | 174 |
| N5—H5*A*···*Cg*1(N1/C2–C6) | 0.90 | 3.47 | 3.362 (7) | 75 |

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