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# Aqua(2,9-dimethyl-1,10-phenanthroline-$\kappa^2N,N'$)diformato-$\kappa^2O,O';\kappa O$-nickel(II) monohydrate

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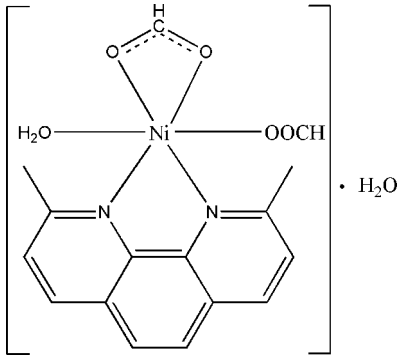
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.006 Å; $R$ factor = 0.035; $wR$ factor = 0.118; data-to-parameter ratio = 16.7.

The asymmetric unit of the title compound, $[Ni(HCO_2)_2(C_{14}H_{12}N_2)(H_2O)]\cdot H_2O$, contains a mononuclear complex molecule hydrogen bonded to a lattice water molecule. The $Ni^{II}$ atom exhibits a distorted octahedral coordination geometry formed by the N atoms from a 2,9-dimethyl-1,10-phenanthroline ligand, two O atoms of a chelating formate anion, one aqua O atom and one O atom of a coordinating formate anion. The molecules are assembled into chains extending along [100] through by O—H···O hydrogen bonds. The supramolecular chains are further linked into layers parallel to (011) by weak $\pi$–$\pi$ packing interactions [centroid–centroid separation = 3.768 (2) Å]. The resulting layers are stacked to meet the requirement of close-packing patterns.

## Related literature

For general background to supramolecular architectures, see: Moulton & Zaworotko (2001); Aakeroy & Seddon (1993). For related structures, see: Go *et al.* (2004); Wang *et al.* (2006); Ni *et al.* (2011).




## Experimental

### Crystal data

$[Ni(HCO_2)_2(C_{14}H_{12}N_2)(H_2O)]\cdot H_2O$
$M_r$ = 393.03
Triclinic, $P\overline{1}$
$a$ = 7.3992 (15) Å
$b$ = 10.373 (2) Å
$c$ = 11.442 (2) Å
$\alpha$ = 82.42 (3)°
$\beta$ = 81.77 (3)°
$\gamma$ = 76.10 (3)°
$V$ = 839.3 (3) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.19 mm$^{-1}$
$T$ = 298 K
0.30 × 0.20 × 0.15 mm

### Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.750, $T_{max}$ = 0.821
8265 measured reflections
3785 independent reflections
3214 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.025

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.118
$S$ = 1.22
3785 reflections
226 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.69 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.67 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O5—H51···O4$^{i}$ | 0.86 | 1.85 | 2.703 (3) | 173.3 |
| O5—H52···O6$^{ii}$ | 0.84 | 2.03 | 2.808 (4) | 154.2 |
| O6—H61···O2$^{iii}$ | 0.85 | 1.98 | 2.830 (4) | 179.3 |
| O6—H62···O3$^{iv}$ | 0.85 | 2.43 | 3.077 (4) | 133.4 |

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZK2016).

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# supporting information

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# Aqua(2,9-dimethyl-1,10-phenanthroline-$\kappa^2N,N'$)diformato-$\kappa^2O,O';\kappa O$-nickel(II) monohydrate

**Ping Xia, Jian-Li Lin and Sheng-Liang Ni**

## S1. Comment

In the past decade, a variety of supramolecular architectures based on non–covalent intermolecular interactions such as hydrogen bonding, van der Walls forces and $\pi$–$\pi$ interactions have been achieved by using transition metal centers and organic ligands due to their possible intriguing structural topologies and potential applications in optics, catalysis, ion exchange, gas storage, and the molecular–based magnetic materials (Aakeroy & Seddon, 1993). Carboxylate ligands have been actively utilized as construction units to obtain lots of supramolecular complexes (Moulton & Zaworotko, 2001). In the paper, we are interested in self–assemblies of $Ni^{II}$ ions and 2,9′–dimethyl–1,10′–phenanthroline with formic acid, leading to successful preparation of a complex $[Ni(HCO_2)_2(C_{14}H_{12}N_2)(H_2O)].H_2O$. The asymmetric unit of the title compound consists of one $Ni^{II}$ ion, one $H_2O$ molecule, one 2,9′–dimethyl–1,10′–phenanthroline molecule, one O,*O*′–chelated formate anion and another coordinated formate anion, and one lattice $H_2O$ molecule(Fig. 1). It's worth to mention, the tetragonal plane is built up by a pair of bidentate formate anions using carboxyl oxygen atoms (Ni–O1 = 2.148 (3) Å, Ni–O2 = 2.150 (3) Å) and by a neutral 2,9′–dimethyl–1,10′–phenanthroline molecule using nitrogen atoms(Ni–N1 = 2.087 (3) Å, Ni–N2 = 2.076 (3) Å).(Table.1). The four atoms around $Ni^{II}$ are almost coplanar and show deviations from -0.093 (2) to 0.092 (2) Å with the average plane, the axial positions are occupied by a pair of oxygen originating from $H_2O$ (Ni–O5 = 2.067 (3) Å) and formate anion (Ni–O3 = 2.046 (2) Å), significantly shorter than the Ni–O1 or Ni–O2 bond distance, which are similar to those observed in related complexes with carboxylate complexes(Go *et al.*, 2004; Wang *et al.*, 2006; Ni *et al.*, 2011). The selected bond angles of O1–Ni–O2, N1–Ni–N2, O3–Ni–O5 are 81.5 (1) °, 61.0 (1) °, and 175.9 (1) °, respectively. For two formate anions, the angle (O1–C1–O2, 122.0 (3) °) of chelated formate is smaller than coordinated (O3–C2–O4, 127.6 (3) Å). The 2,9′–dimethyl–1, 10′–phenanthroline ligand are almost coplanar with the mean square deviations 0.0158 Å, the water molecule is not coordinated to Ni atom and the distance between nickel and water oxygen atom of 7.146 (2) Å.

The molecules are assembled into one-dimensional chains extending along the [100] direction through O5–H51···O4$^{\#1}$, O5–H52···O6$^{\#2}$, O6–H61···O2$^{\#3}$ and O6–H61···O3$^{\#4}$ hydrogen bonds(#1 = $x$ + 1, $y$, $z$; #2 = -$x$ + 2, -$y$, -$z$ + 1; #3 = $x$, $y$, $z$ - 1; #4 = -$x$ + 1, -$y$, -$z$ + 1)(Table.2), the double chains are further linked into two-dimensional layers which parallel to (011) by weak $\pi$–$\pi$ packing interaction(ring centroid separation, 3.768 (2) Å).(Fig. 2). The resulting layers are stacked to meet the requirement of close–packing patterns.

## S2. Experimental

Dropwise addition of 2.0 ml of 1.0 mol.l$^{-1}$ aqueous $Na_2CO_3$ to a stirred aqueous solation of $NiSO_4.7H_2O$ (0.2876 g, 1.0 mmol) in 5.0 ml $H_2O$ produced a green precipitate, $Ni(OH)_{2-2x}(CO_3)_x.yH_2O$, which was centrifuged and washed with water until no $SO_4^{2-}$ anions were detected in the supernatant. The precipitate was added to a stirred aqueous ethanolic solution of 2,9′–dimethyl–1,10′–phenanthroline in 15 ml EtOH–$H_2O$ (2:1,*v*/*v*). And then, 2.0 ml of 1.0 mol.l$^{-1}$aqueous

formalic acid was dropwise added to above mixture and stirred continuously until dissolved of the green precipitate. The green solution (pH = 3.37) was allowed to stand at room temperature. Slow evaporation during two weeks afforded green block crystals(yield:42%).

### S3. Refinement

All H–atoms bonded to C were positioned geometrically and refined using a riding model with d(C–H) = 0.093 Å calculated positionand were refined using a riding, $U_{iso}$(H) = 1.2 $U_{eq}$(C) for aromatic, 0.93 Å, $U_{iso}$(H) = 1.2 $U_{eq}$(C) for CH and 0.96 Å, $U_{iso}$(H) = 1.5 $U_{eq}$(C) for $CH_3$ atoms. H atoms attached to O atoms were found in a difference Fourier synthesisand were refined using a riding model, with the O–H distances fixed as initially found and with $U_{iso}$(H) values set at 1.2 *U*eq(O).

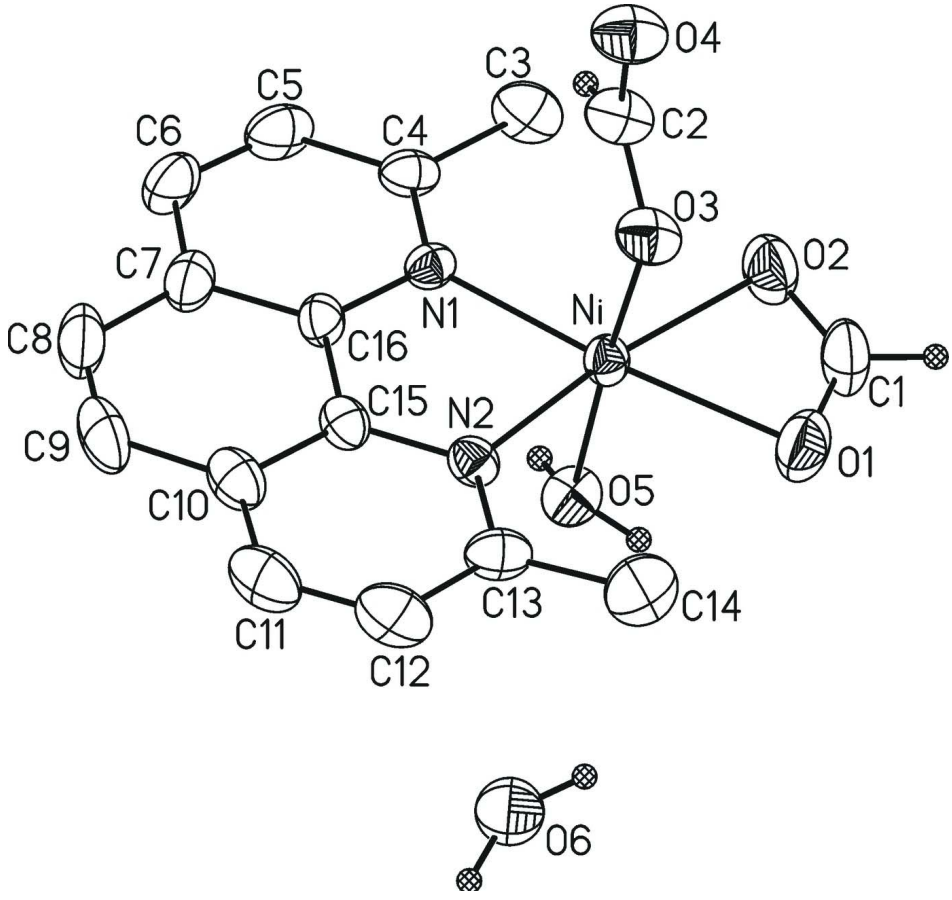


**Figure 1**

*ORTEP* view of the title compound. The dispalcement ellipsoids are drawn at 45% probability level.

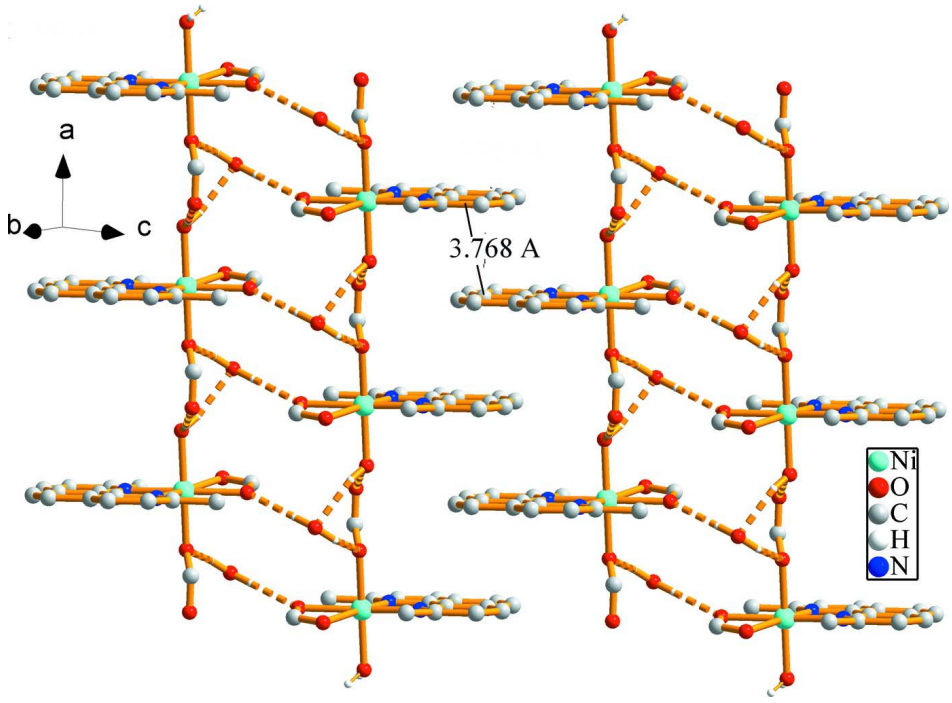


**Figure 2**

two-dimensional layer structure link through hydrogen bonds and $\pi$–$\pi$ packing interactions of the title compound

**Aqua(2,9′-dimethyl-1,10′-phenanthroline-$\kappa^2N,N'$)diformato- $\kappa^2O,O';\kappa O$-nickel(II) monohydrate**

*Crystal data*

$[Ni(HCO_2)_2(C_{14}H_{12}N_2)(H_2O)]\cdot H_2O$
$M_r = 393.03$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.3992\ (15)$ Å
$b = 10.373\ (2)$ Å
$c = 11.442\ (2)$ Å
$\alpha = 82.42\ (3)°$
$\beta = 81.77\ (3)°$
$\gamma = 76.10\ (3)°$
$V = 839.3\ (3)$ Å$^3$
$Z = 2$
$F(000) = 408$
$D_x = 1.555$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3.1$–$27.4°$
$\mu = 1.19$ mm$^{-1}$
$T = 298$ K
Block, green
0.30 × 0.20 × 0.15 mm

*Data collection*

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.750$, $T_{max} = 0.821$
8265 measured reflections
3785 independent reflections
3214 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.4°$, $\theta_{min} = 3.1°$
$h = -9\rightarrow8$
$k = -13\rightarrow13$
$l = -14\rightarrow14$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.118$
$S = 1.22$
3785 reflections
226 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
$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2 + 1.2744P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.69$ e Å$^{-3}$
$\Delta\rho_{min} = -0.67$ e Å$^{-3}$
Extinction correction: *SHELXL*
Extinction coefficient: 0.0015 (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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Ni | 0.77473 (5) | 0.18268 (4) | 0.77154 (3) | 0.02776 (13) |
| O1 | 0.8178 (4) | −0.0310 (2) | 0.7920 (3) | 0.0540 (7) |
| O2 | 0.7827 (4) | 0.0786 (3) | 0.9468 (2) | 0.0494 (6) |
| C1 | 0.8093 (6) | −0.0283 (4) | 0.9011 (4) | 0.0535 (10) |
| H1A | 0.8232 | −0.1082 | 0.9500 | 0.064* |
| O3 | 0.4915 (3) | 0.1977 (2) | 0.7917 (2) | 0.0395 (5) |
| O4 | 0.2105 (3) | 0.3030 (3) | 0.8671 (2) | 0.0485 (6) |
| C2 | 0.3833 (5) | 0.2772 (4) | 0.8554 (3) | 0.0418 (8) |
| H2A | 0.4386 | 0.3228 | 0.8997 | 0.050* |
| O5 | 1.0628 (3) | 0.1559 (2) | 0.7442 (2) | 0.0378 (5) |
| H52 | 1.1256 | 0.0773 | 0.7581 | 0.045* |
| H51 | 1.1024 | 0.2025 | 0.7876 | 0.045* |
| O6 | 0.6484 (4) | 0.0613 (3) | 0.1914 (2) | 0.0544 (7) |
| H61 | 0.6881 | 0.0662 | 0.1176 | 0.065* |
| H62 | 0.5887 | 0.0096 | 0.2356 | 0.065* |
| N1 | 0.7660 (3) | 0.3828 (2) | 0.7853 (2) | 0.0271 (5) |
| N2 | 0.7565 (4) | 0.2549 (3) | 0.5945 (2) | 0.0296 (5) |
| C3 | 0.7791 (6) | 0.3669 (4) | 0.9991 (3) | 0.0460 (9) |
| H3A | 0.7739 | 0.2766 | 0.9924 | 0.069* |
| H3B | 0.6727 | 0.4074 | 1.0509 | 0.069* |
| H3C | 0.8922 | 0.3672 | 1.0310 | 0.069* |
| C4 | 0.7770 (4) | 0.4441 (3) | 0.8789 (3) | 0.0334 (7) |
| C5 | 0.7852 (5) | 0.5793 (4) | 0.8660 (4) | 0.0456 (9) |

| | | | | |
|---|---|---|---|---|
| H5A | 0.7951 | 0.6194 | 0.9321 | 0.055* |
| C6 | 0.7789 (6) | 0.6518 (4) | 0.7588 (4) | 0.0493 (9) |
| H6A | 0.7825 | 0.7415 | 0.7516 | 0.059* |
| C7 | 0.7668 (5) | 0.5908 (3) | 0.6584 (3) | 0.0393 (7) |
| C8 | 0.7604 (6) | 0.6596 (4) | 0.5418 (4) | 0.0530 (10) |
| H8A | 0.7629 | 0.7496 | 0.5305 | 0.064* |
| C9 | 0.7509 (6) | 0.5968 (4) | 0.4485 (4) | 0.0527 (10) |
| H9A | 0.7458 | 0.6441 | 0.3736 | 0.063* |
| C10 | 0.7485 (5) | 0.4584 (4) | 0.4624 (3) | 0.0412 (8) |
| C11 | 0.7418 (6) | 0.3871 (5) | 0.3671 (3) | 0.0530 (10) |
| H11A | 0.7382 | 0.4300 | 0.2906 | 0.064* |
| C12 | 0.7406 (6) | 0.2557 (5) | 0.3877 (3) | 0.0530 (10) |
| H12A | 0.7360 | 0.2085 | 0.3249 | 0.064* |
| C13 | 0.7465 (5) | 0.1901 (4) | 0.5032 (3) | 0.0392 (7) |
| C14 | 0.7372 (7) | 0.0465 (4) | 0.5273 (4) | 0.0602 (11) |
| H14A | 0.7439 | 0.0183 | 0.6102 | 0.090* |
| H14B | 0.8404 | −0.0066 | 0.4815 | 0.090* |
| H14C | 0.6214 | 0.0358 | 0.5057 | 0.090* |
| C15 | 0.7550 (4) | 0.3872 (3) | 0.5750 (3) | 0.0306 (6) |
| C16 | 0.7622 (4) | 0.4551 (3) | 0.6761 (3) | 0.0301 (6) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni | 0.0320 (2) | 0.0254 (2) | 0.0280 (2) | −0.01022 (15) | −0.00438 (15) | −0.00207 (14) |
| O1 | 0.078 (2) | 0.0316 (13) | 0.0548 (17) | −0.0161 (13) | −0.0093 (14) | −0.0044 (11) |
| O2 | 0.0675 (18) | 0.0447 (15) | 0.0364 (13) | −0.0178 (13) | −0.0080 (12) | 0.0058 (11) |
| C1 | 0.070 (3) | 0.0368 (19) | 0.052 (2) | −0.0164 (18) | −0.0105 (19) | 0.0139 (17) |
| O3 | 0.0273 (11) | 0.0512 (14) | 0.0448 (13) | −0.0162 (10) | −0.0022 (10) | −0.0107 (11) |
| O4 | 0.0317 (13) | 0.0651 (17) | 0.0524 (15) | −0.0129 (12) | −0.0027 (11) | −0.0177 (13) |
| C2 | 0.0361 (18) | 0.056 (2) | 0.0394 (18) | −0.0179 (16) | −0.0018 (14) | −0.0144 (16) |
| O5 | 0.0293 (11) | 0.0398 (12) | 0.0462 (13) | −0.0070 (9) | −0.0104 (10) | −0.0054 (10) |
| O6 | 0.0642 (18) | 0.0550 (16) | 0.0460 (15) | −0.0148 (14) | −0.0076 (13) | −0.0080 (12) |
| N1 | 0.0247 (12) | 0.0272 (12) | 0.0303 (12) | −0.0059 (10) | −0.0023 (9) | −0.0072 (9) |
| N2 | 0.0316 (13) | 0.0338 (13) | 0.0248 (12) | −0.0104 (11) | −0.0033 (10) | −0.0028 (10) |
| C3 | 0.052 (2) | 0.061 (2) | 0.0322 (17) | −0.0201 (18) | −0.0079 (15) | −0.0130 (16) |
| C4 | 0.0290 (15) | 0.0397 (17) | 0.0350 (16) | −0.0114 (13) | 0.0011 (12) | −0.0147 (13) |
| C5 | 0.045 (2) | 0.045 (2) | 0.054 (2) | −0.0166 (16) | 0.0011 (16) | −0.0251 (17) |
| C6 | 0.054 (2) | 0.0294 (17) | 0.067 (3) | −0.0139 (16) | 0.0035 (19) | −0.0152 (16) |
| C7 | 0.0356 (17) | 0.0284 (16) | 0.053 (2) | −0.0085 (13) | −0.0034 (15) | −0.0005 (14) |
| C8 | 0.057 (2) | 0.0317 (18) | 0.066 (3) | −0.0117 (17) | −0.005 (2) | 0.0130 (17) |
| C9 | 0.056 (2) | 0.052 (2) | 0.045 (2) | −0.0155 (19) | −0.0094 (18) | 0.0235 (18) |
| C10 | 0.0361 (18) | 0.050 (2) | 0.0353 (17) | −0.0103 (15) | −0.0067 (14) | 0.0071 (15) |
| C11 | 0.057 (2) | 0.075 (3) | 0.0253 (17) | −0.014 (2) | −0.0086 (16) | 0.0037 (17) |
| C12 | 0.062 (3) | 0.074 (3) | 0.0280 (17) | −0.021 (2) | −0.0083 (16) | −0.0125 (17) |
| C13 | 0.0382 (18) | 0.0484 (19) | 0.0346 (17) | −0.0101 (15) | −0.0039 (13) | −0.0165 (14) |
| C14 | 0.085 (3) | 0.057 (2) | 0.052 (2) | −0.030 (2) | −0.009 (2) | −0.0245 (19) |
| C15 | 0.0275 (15) | 0.0337 (15) | 0.0304 (15) | −0.0087 (12) | −0.0043 (12) | 0.0016 (12) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C16 | 0.0304 (15) | 0.0274 (14) | 0.0335 (15) | −0.0106 (12) | −0.0021 (12) | −0.0006 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ni—O3 | 2.046 (2) | C3—H3C | 0.9600 |
| Ni—O5 | 2.066 (2) | C4—C5 | 1.405 (5) |
| Ni—N2 | 2.076 (2) | C5—C6 | 1.352 (6) |
| Ni—N1 | 2.087 (2) | C5—H5A | 0.9300 |
| Ni—O1 | 2.148 (3) | C6—C7 | 1.406 (5) |
| Ni—O2 | 2.150 (2) | C6—H6A | 0.9300 |
| Ni—C1 | 2.457 (4) | C7—C16 | 1.403 (4) |
| O1—C1 | 1.244 (5) | C7—C8 | 1.429 (5) |
| O2—C1 | 1.249 (5) | C8—C9 | 1.341 (6) |
| C1—H1A | 0.9300 | C8—H8A | 0.9300 |
| O3—C2 | 1.235 (4) | C9—C10 | 1.428 (5) |
| O4—C2 | 1.233 (4) | C9—H9A | 0.9300 |
| C2—H2A | 0.9300 | C10—C15 | 1.399 (4) |
| O5—H52 | 0.8426 | C10—C11 | 1.408 (5) |
| O5—H51 | 0.8597 | C11—C12 | 1.354 (6) |
| O6—H61 | 0.8524 | C11—H11A | 0.9300 |
| O6—H62 | 0.8469 | C12—C13 | 1.406 (5) |
| N1—C4 | 1.337 (4) | C12—H12A | 0.9300 |
| N1—C16 | 1.370 (4) | C13—C14 | 1.495 (5) |
| N2—C13 | 1.334 (4) | C14—H14A | 0.9600 |
| N2—C15 | 1.359 (4) | C14—H14B | 0.9600 |
| C3—C4 | 1.497 (5) | C14—H14C | 0.9600 |
| C3—H3A | 0.9600 | C15—C16 | 1.444 (4) |
| C3—H3B | 0.9600 | | |
| | | | |
| O3—Ni—O5 | 175.85 (9) | C4—C3—H3C | 109.5 |
| O3—Ni—N2 | 88.19 (10) | H3A—C3—H3C | 109.5 |
| O5—Ni—N2 | 90.52 (10) | H3B—C3—H3C | 109.5 |
| O3—Ni—N1 | 97.19 (10) | N1—C4—C5 | 121.0 (3) |
| O5—Ni—N1 | 86.51 (10) | N1—C4—C3 | 119.0 (3) |
| N2—Ni—N1 | 81.48 (10) | C5—C4—C3 | 119.9 (3) |
| O3—Ni—O1 | 89.42 (11) | C6—C5—C4 | 121.0 (3) |
| O5—Ni—O1 | 87.32 (11) | C6—C5—H5A | 119.5 |
| N2—Ni—O1 | 110.07 (11) | C4—C5—H5A | 119.5 |
| N1—Ni—O1 | 166.96 (10) | C5—C6—C7 | 119.6 (3) |
| O3—Ni—O2 | 88.37 (11) | C5—C6—H6A | 120.2 |
| O5—Ni—O2 | 92.29 (11) | C7—C6—H6A | 120.2 |
| N2—Ni—O2 | 170.43 (10) | C16—C7—C6 | 117.0 (3) |
| N1—Ni—O2 | 107.82 (10) | C16—C7—C8 | 119.6 (3) |
| O1—Ni—O2 | 60.97 (11) | C6—C7—C8 | 123.4 (3) |
| O3—Ni—C1 | 88.83 (13) | C9—C8—C7 | 121.2 (3) |
| O5—Ni—C1 | 89.66 (13) | C9—C8—H8A | 119.4 |
| N2—Ni—C1 | 140.41 (13) | C7—C8—H8A | 119.4 |
| N1—Ni—C1 | 138.01 (12) | C8—C9—C10 | 120.9 (3) |

| | | | |
|---|---|---|---|
| O1—Ni—C1 | 30.42 (12) | C8—C9—H9A | 119.6 |
| O2—Ni—C1 | 30.54 (12) | C10—C9—H9A | 119.6 |
| C1—O1—Ni | 88.6 (2) | C15—C10—C11 | 117.1 (3) |
| C1—O2—Ni | 88.4 (2) | C15—C10—C9 | 119.7 (3) |
| O1—C1—O2 | 122.0 (3) | C11—C10—C9 | 123.2 (3) |
| O1—C1—Ni | 60.93 (19) | C12—C11—C10 | 119.6 (3) |
| O2—C1—Ni | 61.03 (18) | C12—C11—H11A | 120.2 |
| O1—C1—H1A | 119.0 | C10—C11—H11A | 120.2 |
| O2—C1—H1A | 119.0 | C11—C12—C13 | 120.5 (3) |
| Ni—C1—H1A | 179.7 | C11—C12—H12A | 119.8 |
| C2—O3—Ni | 121.6 (2) | C13—C12—H12A | 119.8 |
| O4—C2—O3 | 127.6 (3) | N2—C13—C12 | 121.0 (3) |
| O4—C2—H2A | 116.2 | N2—C13—C14 | 118.2 (3) |
| O3—C2—H2A | 116.2 | C12—C13—C14 | 120.8 (3) |
| Ni—O5—H52 | 116.4 | C13—C14—H14A | 109.5 |
| Ni—O5—H51 | 111.9 | C13—C14—H14B | 109.5 |
| H52—O5—H51 | 104.9 | H14A—C14—H14B | 109.5 |
| H61—O6—H62 | 132.8 | C13—C14—H14C | 109.5 |
| C4—N1—C16 | 118.4 (3) | H14A—C14—H14C | 109.5 |
| C4—N1—Ni | 130.5 (2) | H14B—C14—H14C | 109.5 |
| C16—N1—Ni | 110.88 (19) | N2—C15—C10 | 122.9 (3) |
| C13—N2—C15 | 118.9 (3) | N2—C15—C16 | 117.6 (3) |
| C13—N2—Ni | 129.2 (2) | C10—C15—C16 | 119.5 (3) |
| C15—N2—Ni | 111.95 (19) | N1—C16—C7 | 123.0 (3) |
| C4—C3—H3A | 109.5 | N1—C16—C15 | 118.0 (3) |
| C4—C3—H3B | 109.5 | C7—C16—C15 | 119.0 (3) |
| H3A—C3—H3B | 109.5 | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O5—H51···O4$^{i}$ | 0.86 | 1.85 | 2.703 (3) | 173.3 |
| O5—H52···O6$^{ii}$ | 0.84 | 2.03 | 2.808 (4) | 154.2 |
| O6—H61···O2$^{iii}$ | 0.85 | 1.98 | 2.830 (4) | 179.3 |
| O6—H62···O3$^{iv}$ | 0.85 | 2.43 | 3.077 (4) | 133.4 |

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