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# [*N*,*N*,*N*′,*N*′-Tetrakis(benzimidazol-2-ylmethyl)cyclohexane-1,2-diamine]nickel(II) dinitrate dihydrate

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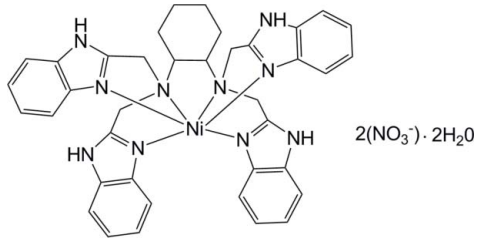
Key indicators: single-crystal X-ray study; $T$ = 292 K; mean $\sigma$(C–C) = 0.005 Å; H-atom completeness 91%; disorder in solvent or counterion; $R$ factor = 0.056; $wR$ factor = 0.133; data-to-parameter ratio = 12.7.

In the title compound, $[Ni(C_{38}H_{38}N_{10})](NO_3)_2\cdot 2H_2O$, the $Ni^{II}$ ion is located on a crystallographic twofold rotation axis and is in a distorted octahedral coordination environment. The crystal structure is stablized by intermolecular N—H···O and C—H···O hydrogen bonds, and weak C—H···$\pi$ interactions. The O atoms of the unique nitrate ion are disordered over two sites with occupancies of 0.63 (1) and 0.37 (1). In addition, the O atom of the unique solvent water molecule is disorded over two sites with equal occupancies.

## Related literature

For background information, see: Oki *et al.* (1996); Hendriks *et al.* (1982); Main (1992); Zhao *et al.* (2005). For the structure of the free ligand of the title compound, see: Li *et al.* (2005).




## Experimental

### Crystal data

$[Ni(C_{38}H_{38}N_{10})](NO_3)_2\cdot 2H_2O$
$M_r$ = 853.55
Monoclinic, $C2/c$
$a$ = 15.3395 (16) Å
$b$ = 13.1695 (14) Å
$c$ = 19.606 (2) Å
$\beta$ = 98.501 (2)°
$V$ = 3917.2 (7) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.56 mm$^{-1}$
$T$ = 292 (2) K
0.32 × 0.20 × 0.10 mm

### Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.840, $T_{max}$ = 0.946
10917 measured reflections
3847 independent reflections
2618 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.074

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.133
$S$ = 0.95
3847 reflections
303 parameters
65 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.43 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.34 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Ni1—N2 | 2.061 (2) | Ni1—N1 | 2.190 (3) |
| Ni1—N4 | 2.071 (3) | | |
| N2—Ni1—N2$^{i}$ | 175.20 (15) | N4—Ni1—N1$^{i}$ | 79.11 (10) |
| N2—Ni1—N4 | 90.83 (10) | N2—Ni1—N1 | 94.90 (10) |
| N2—Ni1—N4$^{i}$ | 91.53 (10) | N4—Ni1—N1 | 158.69 (10) |
| N2—Ni1—N1$^{i}$ | 81.44 (10) | N1$^{i}$—Ni1—N1 | 81.47 (14) |

Symmetry code: (i) $-x, y, -z+\frac{3}{2}$.

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

*Cg*1 and *Cg*2 are the centroids defined by atoms C7–C12 and C14–C19, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···O1$^{ii}$ | 0.86 | 1.94 | 2.774 (10) | 165 |
| N5—H5···O2$^{iii}$ | 0.86 | 2.14 | 2.923 (7) | 151 |
| C4—H4*B*···O4 | 0.97 | 2.37 | 3.268 (12) | 154 |
| C11—H11···*Cg*1$^{iv}$ | 0.93 | 2.73 | 3.542 | 147 |
| C16—H16···*Cg*2$^{v}$ | 0.93 | 2.79 | 3.680 | 160 |

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2699).

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# supporting information

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# [*N*,*N*,*N*′,*N*′-Tetrakis(benzimidazol-2-ylmethyl)cyclohexane-1,2-diamine]-nickel(II) dinitrate dihydrate

**Dan Zhan and Zuo-An Xiao**

## S1. Comment

*N*,*N*,*N*′,*N*′-Tetrakis(2-benzimidazolymethyl) cyclohexane-1,2-diamine (CTB) is a polybenzimidazole ligand, which has the advantage that the basicity of the coordinating group approximates that of histidine (pKb: histidine = 7.96 and benzimidazole = 8.47; Main, 1992). Recently, studies of ligand CTB and its metal coordination compounds have been widely carried out (Li *et al.*,2005; Zhao *et al.*, 2005). In a continuation of this work, the title compound, (I), was prepared as part of a series of syntheses to produce new benzimidazole derivatives. We report the crystal stucture of the title compound herein.

In the molecule structure of (I), the $Ni^{II}$ ion is located on a crystallographic twofold rotation axis and is is coordinated by four benzimidazolyl(bzim) N atoms and two amino N atoms of the ligand CTB, in a distorted octahedral environment (Fig.1). The amino N atoms are slightly further away from the $Ni^{II}$ ion than the benzimidazolyl N atoms. The Ni-N bond lengths are similar to the values reported in a related structure (Oki *et al.*,1996). As shown in Fig. 2, the crystal structure is stablized by intermolecular N—H···O, C—H···O hydrogen bonds and weak C—H···$\pi$ interactions.

## S2. Experimental

All reagents and solvents were used as obtained without further purification. The ligand CTB was prepared according to literature methods (Hendriks *et al.*, 1982). Compound (I) was synthesized by refluxing stoichiometric quantities (1:1 molar ratio) of CTB (0.64 g, 1 mmol) and nickel(II) dinitrate hexahydrate (0.29 g, 1 mmol) in 95% ethanol (30 ml) at 333 K for 6 h. The solution was cooled to room temperature, filtered and evaporated to obtain the product (yield 72%). Crystals of (I) were grown from an ethanol solution by slow evaporation.

## S3. Refinement

In (I), the nitrate O atoms are disordered over two positions with the final refined occupancies of 0.63 (1):0.37 (1). Water atom O4 is also disordered over two positions with both the occupancies being set to 0.5. H atoms bonded to water molecules were not located and were not included in the refinement but are included in the molecular formula. All H atoms (except for H3A) were included in geometrical positions with C—H=0.97 Å (methylene), 0.93Å (aromatic), 0.86Å (imine) and all the $U_{iso}$values were set 1.2 times of their carrier atoms. The positional parameters of atom H3A were refined.

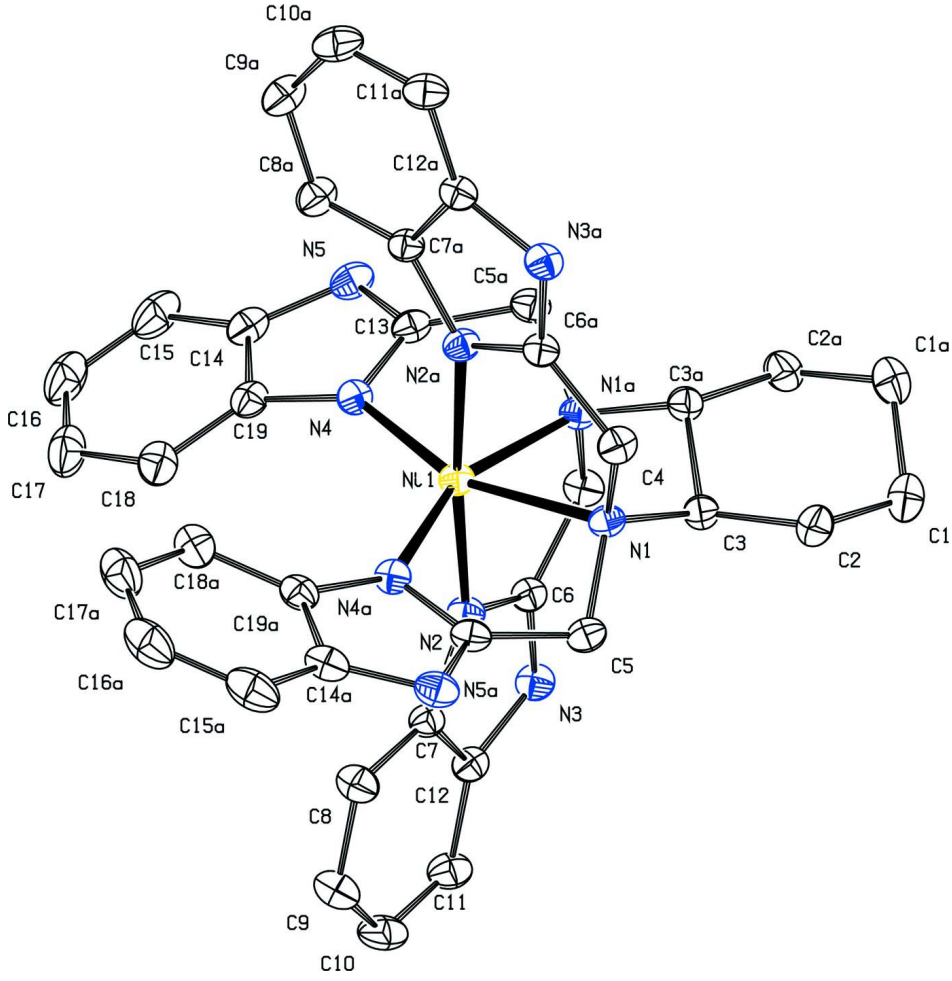


**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The nitrate anions, water molecules and H atoms are omitted for clarity [symmetry code: (a) -x, y, -z+3/2].

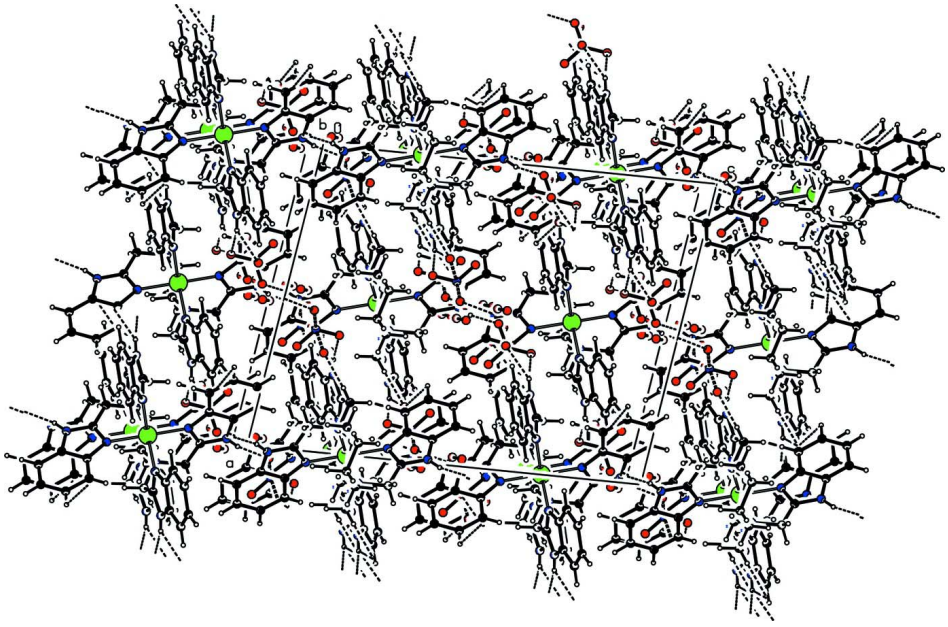

**Figure 2**

Part of the crystal structure showing the linking of molecules by H-bonding and weak C—H···$\pi$ interactions as dashed lines.

**[*N*,*N*,*N*′,*N*′-Tetrakis(benzimidazol-2- ylmethyl)cyclohexane-1,2-diamine]nickel(II) dinitrate dihydrate**

*Crystal data*

$[Ni(C_{38}H_{38}N_{10})](NO_3)_2\cdot 2H_2O$
$M_r = 853.55$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 15.3395\ (16)$ Å
$b = 13.1695\ (14)$ Å
$c = 19.606\ (2)$ Å
$\beta = 98.501\ (2)°$
$V = 3917.2\ (7)$ Å$^3$
$Z = 4$
$F(000) = 1784$
$D_x = 1.447$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2061 reflections
$\theta = 2.4–22.1°$
$\mu = 0.57$ mm$^{-1}$
$T = 292$ K
Plate, purple
0.32 × 0.20 × 0.10 mm

*Data collection*

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.840$, $T_{max} = 0.946$
10917 measured reflections
3847 independent reflections
2618 reflections with $I > 2\sigma(I)$
$R_{int} = 0.074$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.1°$
$h = -18\rightarrow17$
$k = -10\rightarrow16$
$l = -24\rightarrow24$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.133$
$S = 0.95$
3847 reflections
303 parameters
65 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å$^{-3}$
$\Delta\rho_{min} = -0.34$ 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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Ni1 | 0.0000 | 0.06922 (5) | 0.7500 | 0.0383 (2) | |
| N1 | 0.08499 (16) | 0.1952 (2) | 0.79130 (13) | 0.0411 (7) | |
| N2 | 0.03564 (16) | 0.0758 (2) | 0.65276 (12) | 0.0420 (7) | |
| N3 | 0.01367 (17) | 0.1461 (2) | 0.54912 (12) | 0.0461 (7) | |
| H3 | −0.0083 | 0.1852 | 0.5158 | 0.055* | |
| N4 | −0.11459 (17) | −0.0078 (2) | 0.71196 (12) | 0.0419 (7) | |
| N5 | −0.25584 (18) | 0.0113 (3) | 0.66910 (14) | 0.0552 (8) | |
| H5 | −0.3063 | 0.0401 | 0.6586 | 0.066* | |
| N6 | 0.8994 (3) | 0.3077 (5) | 0.4093 (3) | 0.139 (2) | |
| O1 | 0.9736 (6) | 0.2879 (13) | 0.4445 (5) | 0.268 (8) | 0.630 (9) |
| O2 | 0.8880 (3) | 0.3273 (6) | 0.3471 (3) | 0.119 (3) | 0.630 (9) |
| O3 | 0.8392 (5) | 0.3165 (5) | 0.4456 (4) | 0.142 (3) | 0.630 (9) |
| O1′ | 0.9621 (5) | 0.2465 (7) | 0.4281 (4) | 0.058 (3) | 0.370 (9) |
| O2′ | 0.9055 (8) | 0.4029 (8) | 0.4173 (8) | 0.161 (7) | 0.370 (9) |
| O3′ | 0.8270 (19) | 0.2712 (14) | 0.377 (3) | 0.29 (12)* | 0.370 (9) |
| O4 | 0.0215 (8) | 0.4055 (10) | 0.9433 (5) | 0.169 (6) | 0.50 (2) |
| O4′ | 0.0237 (12) | 0.491 (2) | 0.9646 (10) | 0.279 (12) | 0.50 (2) |
| C1 | 0.0479 (3) | 0.4797 (3) | 0.7444 (2) | 0.0738 (12) | |
| H1A | 0.0765 | 0.5412 | 0.7635 | 0.089* | |
| H1B | 0.0512 | 0.4784 | 0.6954 | 0.089* | |
| C2 | 0.0954 (2) | 0.3874 (3) | 0.7790 (2) | 0.0609 (10) | |
| H2A | 0.1560 | 0.3873 | 0.7704 | 0.073* | |
| H2B | 0.0958 | 0.3916 | 0.8284 | 0.073* | |
| C3 | 0.0508 (2) | 0.2889 (3) | 0.75205 (18) | 0.0454 (8) | |
| H3A | 0.063 (2) | 0.280 (2) | 0.7048 (16) | 0.054* | |
| C4 | 0.0837 (2) | 0.2029 (3) | 0.86709 (16) | 0.0494 (9) | |
| H4A | 0.1394 | 0.1790 | 0.8917 | 0.059* | |
| H4B | 0.0767 | 0.2734 | 0.8795 | 0.059* | |
| C5 | 0.1735 (2) | 0.1638 (3) | 0.77788 (18) | 0.0492 (9) | |

| | | | | |
|---|---|---|---|---|
| H5A | 0.2189 | 0.2039 | 0.8052 | 0.059* |
| H5B | 0.1787 | 0.1722 | 0.7295 | 0.059* |
| C6 | −0.0106 (2) | 0.1420 (3) | 0.61190 (15) | 0.0412 (8) |
| C7 | 0.0944 (2) | 0.0319 (3) | 0.61274 (15) | 0.0412 (8) |
| C8 | 0.1581 (2) | −0.0419 (3) | 0.62782 (19) | 0.0570 (10) |
| H8 | 0.1678 | −0.0735 | 0.6707 | 0.068* |
| C9 | 0.2069 (3) | −0.0668 (3) | 0.5766 (2) | 0.0644 (11) |
| H9 | 0.2502 | −0.1165 | 0.5852 | 0.077* |
| C10 | 0.1936 (3) | −0.0204 (3) | 0.51282 (19) | 0.0658 (11) |
| H10 | 0.2289 | −0.0386 | 0.4801 | 0.079* |
| C11 | 0.1299 (2) | 0.0515 (3) | 0.49675 (17) | 0.0561 (10) |
| H11 | 0.1204 | 0.0823 | 0.4536 | 0.067* |
| C12 | 0.0804 (2) | 0.0764 (3) | 0.54747 (15) | 0.0441 (8) |
| C13 | −0.1819 (2) | 0.0548 (3) | 0.70208 (16) | 0.0453 (8) |
| C14 | −0.2356 (2) | −0.0880 (3) | 0.65533 (18) | 0.0546 (10) |
| C15 | −0.2841 (3) | −0.1652 (4) | 0.6196 (2) | 0.0793 (14) |
| H15 | −0.3432 | −0.1566 | 0.6015 | 0.095* |
| C16 | −0.2408 (3) | −0.2551 (4) | 0.6122 (2) | 0.0862 (15) |
| H16 | −0.2710 | −0.3084 | 0.5883 | 0.103* |
| C17 | −0.1518 (3) | −0.2677 (3) | 0.6401 (2) | 0.0800 (14) |
| H17 | −0.1248 | −0.3298 | 0.6346 | 0.096* |
| C18 | −0.1031 (3) | −0.1913 (3) | 0.67524 (18) | 0.0601 (10) |
| H18 | −0.0439 | −0.2002 | 0.6931 | 0.072* |
| C19 | −0.1463 (2) | −0.1002 (3) | 0.68280 (16) | 0.0468 (9) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.0387 (4) | 0.0453 (4) | 0.0307 (3) | 0.000 | 0.0044 (2) | 0.000 |
| N1 | 0.0380 (15) | 0.0490 (17) | 0.0366 (14) | −0.0011 (13) | 0.0062 (11) | 0.0024 (13) |
| N2 | 0.0414 (15) | 0.0507 (17) | 0.0342 (14) | 0.0041 (14) | 0.0066 (11) | 0.0015 (14) |
| N3 | 0.0536 (17) | 0.0550 (18) | 0.0292 (14) | 0.0030 (15) | 0.0044 (12) | 0.0085 (13) |
| N4 | 0.0433 (16) | 0.0469 (17) | 0.0347 (15) | −0.0039 (14) | 0.0028 (12) | −0.0051 (13) |
| N5 | 0.0393 (17) | 0.071 (2) | 0.0544 (19) | −0.0096 (16) | 0.0027 (14) | 0.0030 (17) |
| N6 | 0.087 (4) | 0.119 (5) | 0.203 (8) | 0.000 (4) | −0.007 (5) | 0.038 (5) |
| O1 | 0.179 (10) | 0.317 (15) | 0.290 (14) | 0.021 (10) | −0.025 (9) | 0.206 (12) |
| O2 | 0.079 (4) | 0.176 (7) | 0.097 (4) | 0.031 (4) | −0.003 (3) | 0.091 (5) |
| O3 | 0.127 (6) | 0.125 (6) | 0.191 (7) | 0.023 (5) | 0.082 (5) | −0.025 (5) |
| O1′ | 0.052 (5) | 0.076 (6) | 0.044 (4) | 0.027 (4) | 0.005 (3) | 0.023 (4) |
| O2′ | 0.115 (9) | 0.170 (13) | 0.184 (13) | 0.027 (9) | −0.025 (8) | 0.000 (10) |
| O4 | 0.239 (11) | 0.123 (10) | 0.149 (8) | 0.023 (7) | 0.043 (7) | −0.076 (6) |
| O4′ | 0.311 (17) | 0.28 (2) | 0.247 (17) | 0.064 (15) | 0.042 (12) | 0.007 (16) |
| C1 | 0.084 (3) | 0.050 (2) | 0.088 (3) | −0.011 (2) | 0.013 (3) | −0.001 (2) |
| C2 | 0.061 (2) | 0.053 (2) | 0.069 (3) | −0.011 (2) | 0.012 (2) | −0.003 (2) |
| C3 | 0.0481 (19) | 0.045 (2) | 0.0440 (19) | −0.0006 (17) | 0.0101 (16) | 0.0002 (17) |
| C4 | 0.047 (2) | 0.059 (2) | 0.0403 (19) | −0.0071 (18) | 0.0007 (15) | −0.0039 (17) |
| C5 | 0.0388 (19) | 0.058 (2) | 0.050 (2) | −0.0037 (17) | 0.0064 (15) | 0.0022 (18) |
| C6 | 0.0418 (18) | 0.047 (2) | 0.0339 (17) | −0.0018 (16) | 0.0043 (14) | −0.0007 (16) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C7 | 0.0434 (18) | 0.047 (2) | 0.0335 (17) | −0.0016 (16) | 0.0075 (14) | −0.0021 (15) |
| C8 | 0.060 (2) | 0.063 (3) | 0.049 (2) | 0.013 (2) | 0.0106 (18) | 0.0008 (19) |
| C9 | 0.063 (2) | 0.073 (3) | 0.059 (2) | 0.017 (2) | 0.0133 (19) | −0.008 (2) |
| C10 | 0.060 (3) | 0.094 (3) | 0.047 (2) | −0.002 (2) | 0.0188 (19) | −0.017 (2) |
| C11 | 0.059 (2) | 0.075 (3) | 0.0358 (18) | −0.004 (2) | 0.0118 (17) | −0.0019 (19) |
| C12 | 0.0461 (19) | 0.051 (2) | 0.0345 (17) | −0.0066 (18) | 0.0051 (14) | −0.0027 (16) |
| C13 | 0.0402 (19) | 0.059 (2) | 0.0372 (18) | −0.0065 (18) | 0.0069 (14) | 0.0005 (17) |
| C14 | 0.052 (2) | 0.068 (3) | 0.044 (2) | −0.016 (2) | 0.0081 (17) | 0.0011 (19) |
| C15 | 0.073 (3) | 0.094 (4) | 0.069 (3) | −0.042 (3) | 0.005 (2) | −0.005 (3) |
| C16 | 0.105 (4) | 0.079 (4) | 0.073 (3) | −0.048 (3) | 0.010 (3) | −0.014 (3) |
| C17 | 0.121 (4) | 0.055 (3) | 0.067 (3) | −0.024 (3) | 0.023 (3) | −0.009 (2) |
| C18 | 0.076 (3) | 0.058 (3) | 0.046 (2) | −0.008 (2) | 0.0063 (19) | −0.0029 (19) |
| C19 | 0.057 (2) | 0.053 (2) | 0.0319 (17) | −0.0085 (18) | 0.0091 (15) | 0.0018 (16) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ni1—N2 | 2.061 (2) | C2—H2B | 0.9700 |
| Ni1—N2$^{i}$ | 2.062 (2) | C3—C3$^{i}$ | 1.549 (6) |
| Ni1—N4 | 2.071 (3) | C3—H3A | 0.98 (3) |
| Ni1—N4$^{i}$ | 2.071 (3) | C4—C6$^{i}$ | 1.485 (4) |
| Ni1—N1$^{i}$ | 2.190 (3) | C4—H4A | 0.9700 |
| Ni1—N1 | 2.190 (3) | C4—H4B | 0.9700 |
| N1—C5 | 1.479 (4) | C5—C13$^{i}$ | 1.489 (5) |
| N1—C4 | 1.493 (4) | C5—H5A | 0.9700 |
| N1—C3 | 1.506 (4) | C5—H5B | 0.9700 |
| N2—C6 | 1.318 (4) | C6—C4$^{i}$ | 1.485 (4) |
| N2—C7 | 1.404 (4) | C7—C8 | 1.379 (5) |
| N3—C6 | 1.339 (4) | C7—C12 | 1.395 (4) |
| N3—C12 | 1.378 (4) | C8—C9 | 1.378 (5) |
| N3—H3 | 0.8600 | C8—H8 | 0.9300 |
| N4—C13 | 1.313 (4) | C9—C10 | 1.378 (5) |
| N4—C19 | 1.400 (4) | C9—H9 | 0.9300 |
| N5—C13 | 1.348 (4) | C10—C11 | 1.364 (5) |
| N5—C14 | 1.379 (5) | C10—H10 | 0.9300 |
| N5—H5 | 0.8600 | C11—C12 | 1.378 (4) |
| N6—O2 | 1.233 (6) | C11—H11 | 0.9300 |
| N6—O3 | 1.252 (6) | C13—C5$^{i}$ | 1.489 (5) |
| N6—O2′ | 1.265 (8) | C14—C15 | 1.387 (5) |
| N6—O1′ | 1.267 (7) | C14—C19 | 1.405 (5) |
| N6—O1 | 1.268 (7) | C15—C16 | 1.375 (7) |
| N6—O3′ | 1.286 (9) | C15—H15 | 0.9300 |
| O4′—O4′$^{ii}$ | 1.68 (4) | C16—C17 | 1.403 (6) |
| C1—C1$^{i}$ | 1.519 (8) | C16—H16 | 0.9300 |
| C1—C2 | 1.524 (5) | C17—C18 | 1.376 (5) |
| C1—H1A | 0.9700 | C17—H17 | 0.9300 |
| C1—H1B | 0.9700 | C18—C19 | 1.389 (5) |
| C2—C3 | 1.524 (5) | C18—H18 | 0.9300 |
| C2—H2A | 0.9700 | | |

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| N2—Ni1—N2$^{i}$ | 175.20 (15) | C2—C3—C3$^{i}$ | 114.5 (2) |
| N2—Ni1—N4 | 90.83 (10) | N1—C3—H3A | 106.6 (19) |
| N2$^{i}$—Ni1—N4 | 91.53 (10) | C2—C3—H3A | 106.6 (19) |
| N2—Ni1—N4$^{i}$ | 91.53 (10) | C3$^{i}$—C3—H3A | 106.6 (19) |
| N2$^{i}$—Ni1—N4$^{i}$ | 90.82 (10) | C6$^{i}$—C4—N1 | 111.2 (3) |
| N4—Ni1—N4$^{i}$ | 121.31 (16) | C6$^{i}$—C4—H4A | 109.4 |
| N2—Ni1—N1$^{i}$ | 81.44 (10) | N1—C4—H4A | 109.4 |
| N2$^{i}$—Ni1—N1$^{i}$ | 94.90 (10) | C6$^{i}$—C4—H4B | 109.4 |
| N4—Ni1—N1$^{i}$ | 79.11 (10) | N1—C4—H4B | 109.4 |
| N4$^{i}$—Ni1—N1$^{i}$ | 158.69 (11) | H4A—C4—H4B | 108.0 |
| N2—Ni1—N1 | 94.90 (10) | N1—C5—C13$^{i}$ | 105.6 (3) |
| N2$^{i}$—Ni1—N1 | 81.43 (10) | N1—C5—H5A | 110.6 |
| N4—Ni1—N1 | 158.69 (10) | C13$^{i}$—C5—H5A | 110.6 |
| N4$^{i}$—Ni1—N1 | 79.11 (10) | N1—C5—H5B | 110.6 |
| N1$^{i}$—Ni1—N1 | 81.47 (14) | C13$^{i}$—C5—H5B | 110.6 |
| C5—N1—C4 | 110.1 (2) | H5A—C5—H5B | 108.8 |
| C5—N1—C3 | 113.4 (2) | N2—C6—N3 | 112.8 (3) |
| C4—N1—C3 | 113.5 (3) | N2—C6—C4$^{i}$ | 123.3 (3) |
| C5—N1—Ni1 | 103.5 (2) | N3—C6—C4$^{i}$ | 123.8 (3) |
| C4—N1—Ni1 | 108.93 (19) | C8—C7—C12 | 120.1 (3) |
| C3—N1—Ni1 | 106.76 (18) | C8—C7—N2 | 131.6 (3) |
| C6—N2—C7 | 105.4 (3) | C12—C7—N2 | 108.3 (3) |
| C6—N2—Ni1 | 113.4 (2) | C9—C8—C7 | 117.1 (3) |
| C7—N2—Ni1 | 141.2 (2) | C9—C8—H8 | 121.5 |
| C6—N3—C12 | 107.6 (3) | C7—C8—H8 | 121.5 |
| C6—N3—H3 | 126.2 | C8—C9—C10 | 122.2 (4) |
| C12—N3—H3 | 126.2 | C8—C9—H9 | 118.9 |
| C13—N4—C19 | 105.5 (3) | C10—C9—H9 | 118.9 |
| C13—N4—Ni1 | 110.6 (2) | C11—C10—C9 | 121.4 (3) |
| C19—N4—Ni1 | 142.9 (2) | C11—C10—H10 | 119.3 |
| C13—N5—C14 | 107.4 (3) | C9—C10—H10 | 119.3 |
| C13—N5—H5 | 126.3 | C10—C11—C12 | 116.8 (3) |
| C14—N5—H5 | 126.3 | C10—C11—H11 | 121.6 |
| O2—N6—O3 | 122.3 (5) | C12—C11—H11 | 121.6 |
| O2—N6—O2′ | 85.0 (9) | C11—C12—N3 | 131.8 (3) |
| O3—N6—O2′ | 83.4 (9) | C11—C12—C7 | 122.4 (3) |
| O2—N6—O1′ | 114.3 (7) | N3—C12—C7 | 105.8 (3) |
| O3—N6—O1′ | 119.1 (7) | N4—C13—N5 | 113.0 (3) |
| O2′—N6—O1′ | 123.7 (6) | N4—C13—C5$^{i}$ | 122.1 (3) |
| O2—N6—O1 | 124.5 (6) | N5—C13—C5$^{i}$ | 124.8 (3) |
| O3—N6—O1 | 112.8 (6) | N5—C14—C15 | 132.4 (4) |
| O2′—N6—O1 | 95.3 (11) | N5—C14—C19 | 105.5 (3) |
| O2′—N6—O3′ | 118.3 (7) | C15—C14—C19 | 122.0 (4) |
| O1′—N6—O3′ | 117.9 (7) | C16—C15—C14 | 116.9 (4) |
| O1—N6—O3′ | 146.2 (13) | C16—C15—H15 | 121.5 |
| C1$^{i}$—C1—C2 | 110.1 (3) | C14—C15—H15 | 121.5 |
| C1$^{i}$—C1—H1A | 109.6 | C15—C16—C17 | 121.2 (5) |

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| C2—C1—H1A | 109.6 | C15—C16—H16 | 119.4 |
| C1$^{i}$—C1—H1B | 109.6 | C17—C16—H16 | 119.4 |
| C2—C1—H1B | 109.6 | C18—C17—C16 | 122.3 (5) |
| H1A—C1—H1B | 108.1 | C18—C17—H17 | 118.9 |
| C3—C2—C1 | 111.4 (3) | C16—C17—H17 | 118.9 |
| C3—C2—H2A | 109.4 | C17—C18—C19 | 116.9 (4) |
| C1—C2—H2A | 109.4 | C17—C18—H18 | 121.6 |
| C3—C2—H2B | 109.4 | C19—C18—H18 | 121.6 |
| C1—C2—H2B | 109.4 | C18—C19—N4 | 130.6 (3) |
| H2A—C2—H2B | 108.0 | C18—C19—C14 | 120.8 (4) |
| N1—C3—C2 | 114.5 (3) | N4—C19—C14 | 108.5 (3) |
| N1—C3—C3$^{i}$ | 107.3 (2) | | |

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| N2—Ni1—N1—C5 | −55.5 (2) | Ni1—N1—C5—C13$^{i}$ | −44.1 (3) |
| N2$^{i}$—Ni1—N1—C5 | 127.6 (2) | C7—N2—C6—N3 | −0.9 (4) |
| N4—Ni1—N1—C5 | −160.6 (2) | Ni1—N2—C6—N3 | 179.5 (2) |
| N4$^{i}$—Ni1—N1—C5 | 35.10 (19) | C7—N2—C6—C4$^{i}$ | 177.3 (3) |
| N1$^{i}$—Ni1—N1—C5 | −136.1 (2) | Ni1—N2—C6—C4$^{i}$ | −2.3 (4) |
| N2—Ni1—N1—C4 | −172.7 (2) | C12—N3—C6—N2 | 0.9 (4) |
| N2$^{i}$—Ni1—N1—C4 | 10.5 (2) | C12—N3—C6—C4$^{i}$ | −177.3 (3) |
| N4—Ni1—N1—C4 | 82.3 (3) | C6—N2—C7—C8 | −179.7 (4) |
| N4$^{i}$—Ni1—N1—C4 | −82.0 (2) | Ni1—N2—C7—C8 | −0.2 (6) |
| N1$^{i}$—Ni1—N1—C4 | 106.8 (2) | C6—N2—C7—C12 | 0.5 (4) |
| N2—Ni1—N1—C3 | 64.4 (2) | Ni1—N2—C7—C12 | 180.0 (3) |
| N2$^{i}$—Ni1—N1—C3 | −112.4 (2) | C12—C7—C8—C9 | 1.3 (5) |
| N4—Ni1—N1—C3 | −40.6 (3) | N2—C7—C8—C9 | −178.5 (3) |
| N4$^{i}$—Ni1—N1—C3 | 155.1 (2) | C7—C8—C9—C10 | 0.3 (6) |
| N1$^{i}$—Ni1—N1—C3 | −16.12 (14) | C8—C9—C10—C11 | −1.3 (6) |
| N4—Ni1—N2—C6 | 74.0 (2) | C9—C10—C11—C12 | 0.8 (6) |
| N4$^{i}$—Ni1—N2—C6 | −164.6 (2) | C10—C11—C12—N3 | 178.2 (4) |
| N1$^{i}$—Ni1—N2—C6 | −4.9 (2) | C10—C11—C12—C7 | 0.8 (5) |
| N1—Ni1—N2—C6 | −85.4 (2) | C6—N3—C12—C11 | −178.2 (4) |
| N4—Ni1—N2—C7 | −105.4 (3) | C6—N3—C12—C7 | −0.5 (4) |
| N4$^{i}$—Ni1—N2—C7 | 15.9 (3) | C8—C7—C12—C11 | −1.9 (5) |
| N1$^{i}$—Ni1—N2—C7 | 175.7 (4) | N2—C7—C12—C11 | 178.0 (3) |
| N1—Ni1—N2—C7 | 95.1 (3) | C8—C7—C12—N3 | −179.8 (3) |
| N2—Ni1—N4—C13 | −98.7 (2) | N2—C7—C12—N3 | 0.0 (4) |
| N2$^{i}$—Ni1—N4—C13 | 77.1 (2) | C19—N4—C13—N5 | 0.4 (4) |
| N4$^{i}$—Ni1—N4—C13 | 169.0 (2) | Ni1—N4—C13—N5 | 171.9 (2) |
| N1$^{i}$—Ni1—N4—C13 | −17.6 (2) | C19—N4—C13—C5$^{i}$ | −176.2 (3) |
| N1—Ni1—N4—C13 | 7.0 (4) | Ni1—N4—C13—C5$^{i}$ | −4.6 (4) |
| N2—Ni1—N4—C19 | 67.7 (3) | C14—N5—C13—N4 | −0.7 (4) |
| N2$^{i}$—Ni1—N4—C19 | −116.5 (3) | C14—N5—C13—C5$^{i}$ | 175.7 (3) |
| N4$^{i}$—Ni1—N4—C19 | −24.6 (3) | C13—N5—C14—C15 | −175.8 (4) |
| N1$^{i}$—Ni1—N4—C19 | 148.8 (3) | C13—N5—C14—C19 | 0.7 (4) |
| N1—Ni1—N4—C19 | 173.5 (3) | N5—C14—C15—C16 | 176.1 (4) |
| C1$^{i}$—C1—C2—C3 | 57.5 (5) | C19—C14—C15—C16 | 0.1 (6) |
| C5—N1—C3—C2 | −73.2 (4) | C14—C15—C16—C17 | 0.4 (6) |

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| C4—N1—C3—C2 | 53.5 (4) | C15—C16—C17—C18 | −0.8 (7) |
| Ni1—N1—C3—C2 | 173.5 (2) | C16—C17—C18—C19 | 0.7 (6) |
| C5—N1—C3—C3$^{i}$ | 158.5 (3) | C17—C18—C19—N4 | −176.0 (3) |
| C4—N1—C3—C3$^{i}$ | −74.8 (3) | C17—C18—C19—C14 | −0.1 (5) |
| Ni1—N1—C3—C3$^{i}$ | 45.2 (3) | C13—N4—C19—C18 | 176.4 (3) |
| C1—C2—C3—N1 | −171.0 (3) | Ni1—N4—C19—C18 | 9.6 (6) |
| C1—C2—C3—C3$^{i}$ | −46.4 (5) | C13—N4—C19—C14 | 0.1 (3) |
| C5—N1—C4—C6$^{i}$ | −126.7 (3) | Ni1—N4—C19—C14 | −166.7 (3) |
| C3—N1—C4—C6$^{i}$ | 104.9 (3) | N5—C14—C19—C18 | −177.2 (3) |
| Ni1—N1—C4—C6$^{i}$ | −13.8 (3) | C15—C14—C19—C18 | −0.3 (5) |
| C4—N1—C5—C13$^{i}$ | 72.2 (3) | N5—C14—C19—N4 | −0.5 (4) |
| C3—N1—C5—C13$^{i}$ | −159.4 (3) | C15—C14—C19—N4 | 176.5 (3) |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···O1$^{iii}$ | 0.86 | 1.94 | 2.774 (10) | 165 |
| N5—H5···O2$^{iv}$ | 0.86 | 2.14 | 2.923 (7) | 151 |
| C4—H4*B*···O4 | 0.97 | 2.37 | 3.268 (12) | 154 |
| C11—H11···*Cg*1$^{v}$ | 0.93 | 2.73 | 3.542 | 147 |
| C16—H16···*Cg*2$^{vi}$ | 0.93 | 2.79 | 3.680 | 160 |

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