

# Synthesis, crystal structure and Hirshfeld surface analysis of a 1D coordination polymer *catena*-poly[[diaquabis(nicotinamide- $\kappa N^1$ )nickel(II)]- $\mu$ -fumarato- $\kappa^2 O^1:O^4$ ]

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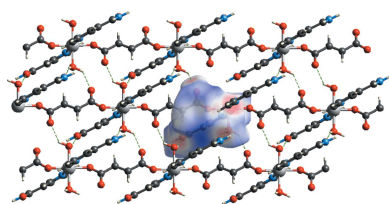
The reaction of NiCl<sub>2</sub> with fumaric acid and nicotinamide in basic solution produces the title polymeric complex, [Ni(C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>)(C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>. The Ni<sup>II</sup> cation, located on an inversion centre, is coordinated by two O atoms of the fumarate dianions, two N atoms from nicotinamide ligands and two water molecules in a distorted octahedral fashion. In the crystal, the fumarate dianions bridge the Ni<sup>II</sup> cations, forming polymeric chains propagating along the [101] direction; the polymeric chains are further linked by O—H···O, N—H···O and C—H···O hydrogen bonds, forming a three-dimensional supramolecular architecture. Hirshfeld surface analyses and two-dimensional fingerprint plots were used to analyse the intermolecular interactions present in the crystal, indicating that the most important contributions for the crystal packing are from H···O/O···H (35.9%), H···H (31.7%) and C···C (10.4%) interactions.

## 1. Chemical context

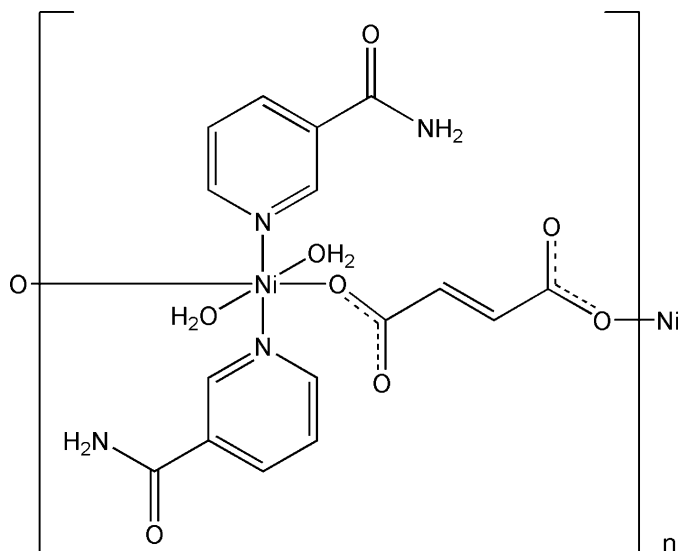
Metal complexes of biologically important ligands are sometimes more effective than the free ligands. Many transition and heavy metal cations play an important role in biological processes in the formation of many vitamins and drug components. An important element for biological systems is nickel. Nickel complexes have biological applications such as antiepileptic, antimicrobial, antibacterial and anticancer activities (Bombicz *et al.*, 2001). The metal-ion geometries of coordination compounds can be easily identified. Dicarboxylic acid ligands are utilized in the synthesis of a range of metal complexes and fumaric acid and amide have been particularly useful in creating many supramolecular structures (Pavlishchuk *et al.*, 2011; Ostrowska *et al.*, 2016), in particular between nicotinamide and a variety of carboxylic acid molecules. We have prepared a new Ni<sup>II</sup> complex, *catena*-poly[[diaquabis(nicotinamide- $\kappa N^1$ )nickel(II)]- $\mu$ -fumarato- $\kappa^2 O^1:O^4$ ], whose structure has been determined by single crystal X-ray diffraction analysis. In addition, to understand the intermolecular interactions in the crystal structure, Hirshfeld surface analysis was performed.

## 2. Structural commentary

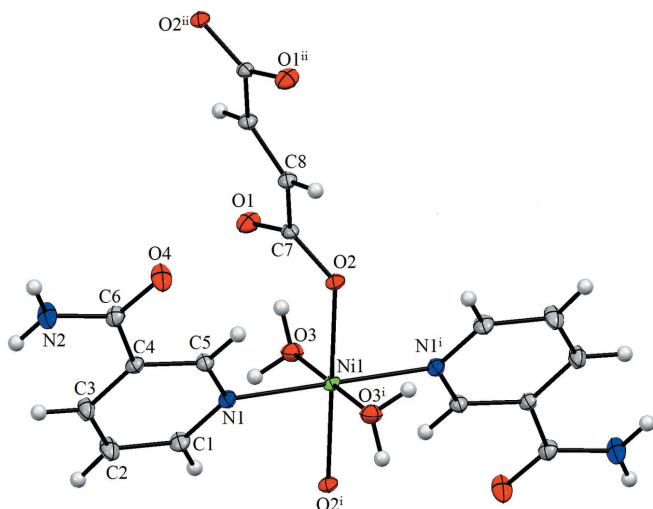
The molecular structure of the asymmetric unit of the title compound is illustrated in Fig. 1. This linear one-dimensional coordination polymer consists of a nickel centre coordinated



in an octahedral fashion by two oxygen atoms of fumaric acid dianions, two nicotinamide nitrogen atoms and two aqua ligands.



The Ni1–O2, Ni1–O3 and Ni1–N1 bond lengths are 2.0484 (12), 2.0792 (13) and 2.1187 (14) Å, respectively. The C–O bond lengths in the deprotonated carboxylic groups differ noticeably [C7–O1 = 1.248 (2) Å and C7–O2 = 1.266 (2) Å], which is typical for monodentately coordinated carboxylates (Gumienna-Kontecka *et al.*, 2007; Pavlishchuk *et al.*, 2010; Penkova *et al.*, 2010). In the same way, the C6–O4 bond in the amide group [1.236 (2) Å] shows partial double-bond character. The values of the Ni–O<sub>water</sub> and Ni–N<sub>pyridine</sub> bond lengths and the bond angles involving the Ni1 atom (see supporting information) are close to those reported for similar nickel(II) complexes (Krämer *et al.*, 2002; Bora & Das, 2011; Moroz *et al.*, 2012). The conformation of the title compound is



**Figure 1**  
The molecular structure of the asymmetric unit of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 20% probability level. [Symmetry codes: (i)  $-x + 1, -y + 2, -z + 2$ ; (ii)  $-x, -y + 1, -z + 2$ .]

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O3–H3A···O4 <sup>ii</sup>	0.85	2.06	2.8699 (19)	159
O3–H3B···O1 <sup>iii</sup>	0.85	2.17	2.8550 (19)	138
O3–H3B···O1 <sup>i</sup>	0.85	2.30	2.9916 (18)	138
N2–H2A···O4 <sup>iv</sup>	0.86	2.16	2.980 (2)	158
N2–H2B···O1 <sup>v</sup>	0.86	2.10	2.929 (2)	161
C3–H3···O1 <sup>v</sup>	0.93	2.40	3.296 (2)	162

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

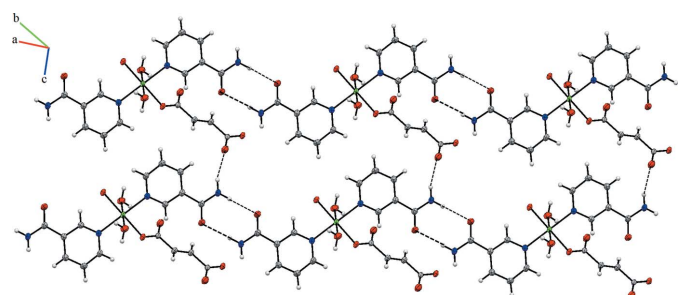
best defined by the torsion angles C4–C5–N1–Ni1, O1–C7–O2–Ni1 and C8–C7–O2–Ni1 of 172.22 (13)°, –26.7 (2)° and 151.80 (11)°, respectively.

### 3. Supramolecular features

In the crystal, the polymeric chains are linked by O–H···O, N–H···O and C–H···O hydrogen bonds (Table 1), forming a three-dimensional supramolecular architecture (Fig. 2). The shortest non-hydrogen-bonding intermolecular distances of the title compound are 2.870 (2) Å [for O3···O4( $-x + 1, -y + 1, -z + 2$ )] and 2.855 (2) Å [for O3···O1( $x + 1, y, z$ )]. The strongest hydrogen-bonded intermolecular distance is 2.06 Å [H3A···O4( $-x + 1, -y + 1, -z + 2$ )].

### 4. Hirshfeld surface analysis

The Hirshfeld surface analysis was performed using the *CrystalExplorer* program (Turner *et al.*, 2017). The Hirshfeld surfaces and their associated two-dimensional fingerprint plots were used to quantify the various intermolecular interactions in the synthesized complex. The Hirshfeld surfaces mapped over  $d_{\text{norm}}$ ,  $d_i$  and  $d_e$  are shown in Fig. 3. The red spots indicate the intermolecular contacts associated with strong hydrogen bonds and interatomic contacts (Gümüş *et al.*, 2018; Kansız & Dege, 2018; Sen *et al.*, 2018). For the title compound, these correspond to the near-type H···O contacts resulting from O–H···O and N–H···O hydrogen bonds (Figs. 3 and 4). The Hirshfeld surfaces were generated using a standard (high) surface resolution with the three-dimensional  $d_{\text{norm}}$  surface



**Figure 2**  
A partial view of the crystal packing of the title compound. Dashed lines indicate the hydrogen bonds (see Table 1).

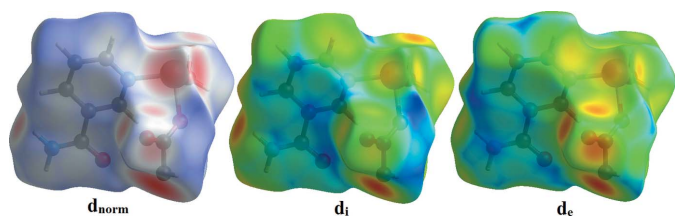


Figure 3  
The Hirshfeld surface of the title compound mapped over  $d_{norm}$ ,  $d_i$  and  $d_e$ .

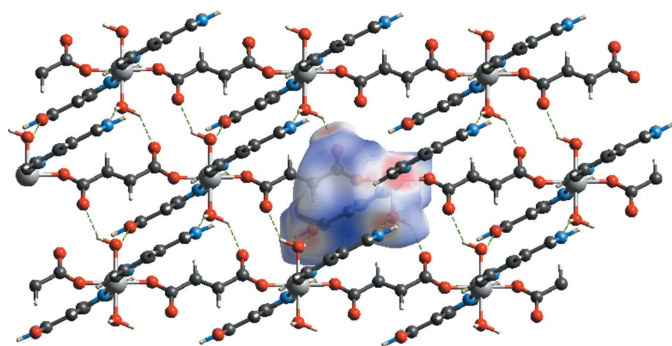


Figure 4  
Hirshfeld surfaces mapped over  $d_{norm}$  to visualize the intermolecular interactions of the title compound.

mapped over a fixed colour scale of  $-1.219$  (red) to  $1.466$  (blue) a.u.

Fig. 5 shows the two-dimensional fingerprint of the sum of the contacts contributing to the Hirshfeld surface represented in normal mode. The graph shown in Fig. 6a represents the  $O \cdots H/H \cdots O$  contacts (35.9%) between the oxygen atoms inside the surface and the hydrogen atoms outside the surface,  $d_e + d_i = 1.9 \text{ \AA}$ , and two symmetrical points at the top, bottom

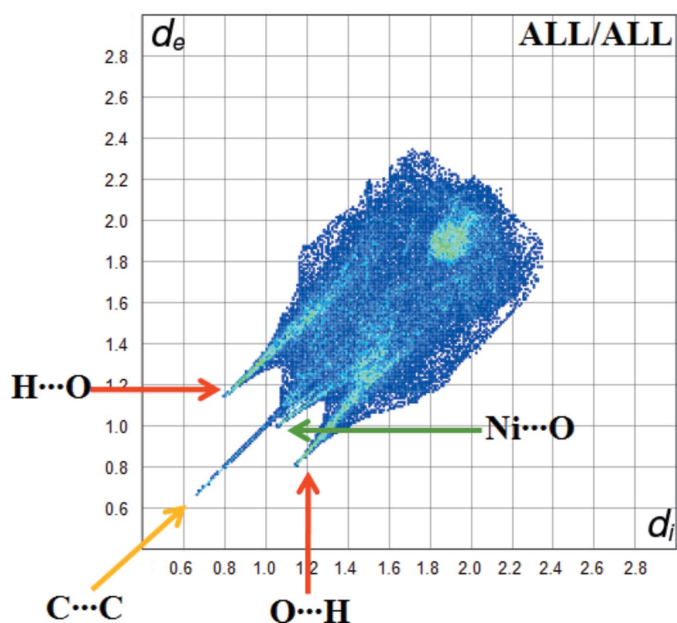


Figure 5  
A fingerprint plot of the title compound.

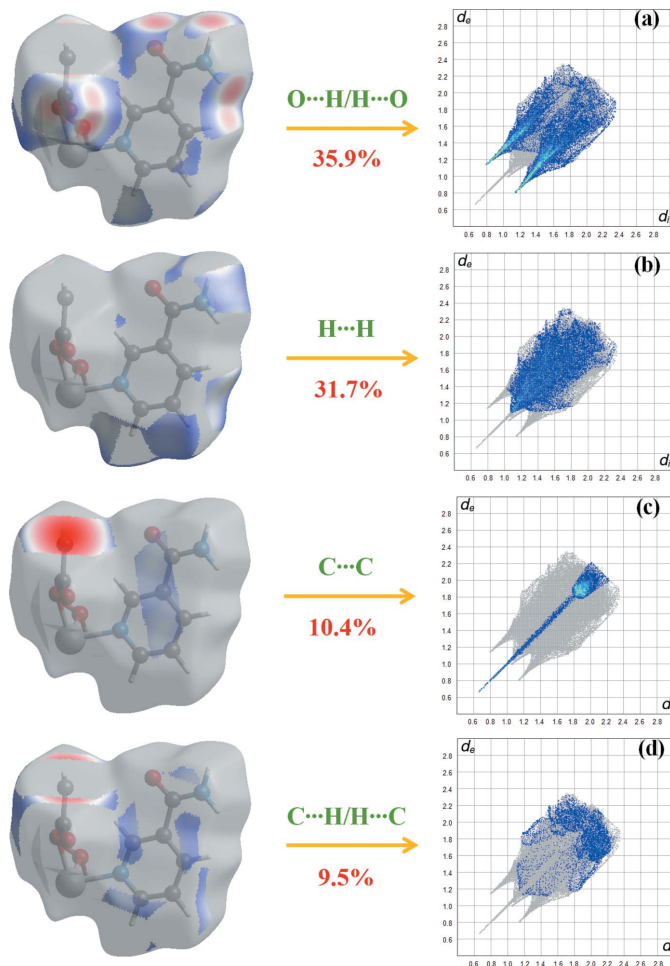


Figure 6  
Two-dimensional fingerprint plots with a  $d_{norm}$  view of the  $O \cdots H/H \cdots O$  (35.9%),  $H \cdots H$  (31.7%),  $C \cdots C$  (10.4%) and  $C \cdots H/H \cdots C$  (9.5%) contacts in the title compound.

left and right. These are characteristic of  $O-H \cdots O$  and  $N-H \cdots O$  hydrogen bonds. Fig. 6b ( $H \cdots H$ ) shows the two-dimensional fingerprint of the ( $d_i$ ,  $d_e$ ) points associated with hydrogen atoms. It is characterized by an end point that points to the origin and corresponds to  $d_i = d_e = 1.08 \text{ \AA}$ , which indicates the presence of the  $H \cdots H$  contacts in this study (31.7%). The graph shown in Fig. 6d ( $C \cdots H/H \cdots C$ ) shows the contact between the carbon atoms inside the surface and the hydrogen atoms outside the Hirshfeld surface and *vice versa* (9.5%). In addition,  $C \cdots C$  (10.4%),  $N \cdots H/H \cdots N$  (3.6%) and  $Ni \cdots O/O \cdots Ni$  (3.4%) contacts contribute to the Hirshfeld surface.

## 5. Synthesis and crystallization

A solution of NaOH (52 mmol, 2.07 g) was added to an aqueous solution of  $H_2Fum$  (26 mmol, 3 g) with stirring. A solution of  $NiCl_2 \cdot 6H_2O$  (26 mmol, 6.14 g) in ethanol was added. The mixture was heated at 353 K for an hour and then the pink mixture was filtered and left to dry at room temperature. The reaction mixture (0.88 mmol, 0.20 g) was

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	[Ni(C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> )(C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]
<i>M<sub>r</sub></i>	453.05
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.3660 (5), 7.5521 (5), 8.9344 (6)
$\alpha$ , $\beta$ , $\gamma$ (°)	109.672 (2), 102.556 (2), 98.887 (2)
<i>V</i> (Å <sup>3</sup> )	442.57 (5)
<i>Z</i>	1
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.15
Crystal size (mm)	0.21 × 0.17 × 0.14
Data collection	
Diffractometer	Stoe <i>IPDS</i> 2
Absorption correction	Analytical ( <i>X-RED32</i> ; Stoe & Cie, 2002)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.622, 0.746
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	20590, 2203, 2075
<i>R<sub>int</sub></i>	0.029
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.669
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.029, 0.076, 1.09
No. of reflections	2203
No. of parameters	134
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.33, -0.51

Computer programs: *X-AREA* (Stoe & Cie, 2002), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2016* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

dissolved in ethanol and added to a methanol solution of nicotinamide (1.76 mmol, 0.21 g). The mixture was heated at 353 K for 30 min with stirring and the resulting suspension was filtered. On slow evaporation of the filtrate, over a period of three weeks, blue block-shaped crystals of the title complex were obtained.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were

positioned geometrically and refined using a riding model: C—H = 0.93 Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

## Acknowledgements

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## supporting information

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## Synthesis, crystal structure and Hirshfeld surface analysis of a 1D coordination polymer *catena*-poly[[diaquabis(nicotinamide- $\kappa N^1$ )nickel(II)]- $\mu$ -fumarato- $\kappa^2 O^1:O^4$ ]

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### Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-AREA* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

*catena*-poly[[diaquabis(nicotinamide- $\kappa N^1$ )nickel(II)]- $\mu$ -fumarato- $\kappa^2 O^1:O^4$ ]

### Crystal data

[Ni(C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>)(C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]

$M_r = 453.05$

Triclinic,  $P\bar{1}$

$a = 7.3660$  (5) Å

$b = 7.5521$  (5) Å

$c = 8.9344$  (6) Å

$\alpha = 109.672$  (2)°

$\beta = 102.556$  (2)°

$\gamma = 98.887$  (2)°

$V = 442.57$  (5) Å<sup>3</sup>

$Z = 1$

$F(000) = 234$

$D_x = 1.700$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9881 reflections

$\theta = 3.0$ – $28.3$ °

$\mu = 1.15$  mm<sup>-1</sup>

$T = 296$  K

Block, blue

$0.21 \times 0.17 \times 0.14$  mm

### Data collection

Stoe IPDS 2

diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: analytical

(X-RED32; Stoe & Cie, 2002)

$T_{\min} = 0.622$ ,  $T_{\max} = 0.746$

20590 measured reflections

2203 independent reflections

2075 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 28.4$ °,  $\theta_{\min} = 2.9$ °

$h = -9 \rightarrow 9$

$k = -10 \rightarrow 10$

$l = -11 \rightarrow 11$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.076$

$S = 1.09$

2203 reflections

134 parameters

0 restraints

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.3311P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.33$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.51$  e Å<sup>-3</sup>



*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.500000	1.000000	1.000000	0.01693 (10)
O2	0.33073 (17)	0.81811 (18)	1.06897 (15)	0.0230 (3)
O1	0.03134 (19)	0.80242 (19)	0.93228 (17)	0.0288 (3)
O3	0.69940 (18)	0.84277 (19)	1.04390 (16)	0.0265 (3)
H3A	0.714414	0.842222	1.140797	0.040*
H3B	0.805970	0.895352	1.036435	0.040*
O4	0.1845 (2)	0.2218 (2)	0.65461 (17)	0.0365 (3)
N1	0.4051 (2)	0.7960 (2)	0.75121 (17)	0.0208 (3)
N2	0.0821 (3)	0.1382 (2)	0.3790 (2)	0.0344 (4)
H2A	0.030092	0.020641	0.362653	0.041*
H2B	0.075841	0.173000	0.296112	0.041*
C8	0.0907 (2)	0.5495 (2)	1.0232 (2)	0.0201 (3)
H8	0.185109	0.498535	1.069060	0.024*
C7	0.1527 (2)	0.7390 (2)	1.00643 (19)	0.0179 (3)
C4	0.2550 (2)	0.4705 (2)	0.5543 (2)	0.0201 (3)
C5	0.3392 (2)	0.6063 (2)	0.7149 (2)	0.0205 (3)
H5	0.350571	0.563601	0.801926	0.025*
C3	0.2450 (3)	0.5333 (3)	0.4242 (2)	0.0280 (4)
H3	0.190437	0.446164	0.314732	0.034*
C6	0.1722 (3)	0.2659 (2)	0.5321 (2)	0.0228 (3)
C1	0.3942 (3)	0.8543 (3)	0.6243 (2)	0.0258 (4)
H1	0.440043	0.985427	0.647565	0.031*
C2	0.3180 (3)	0.7284 (3)	0.4605 (2)	0.0317 (4)
H2	0.315654	0.773682	0.375558	0.038*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.01813 (15)	0.01127 (14)	0.01788 (16)	-0.00304 (10)	0.00371 (11)	0.00516 (11)
O2	0.0213 (6)	0.0206 (6)	0.0234 (6)	-0.0051 (5)	0.0041 (5)	0.0100 (5)
O1	0.0261 (6)	0.0247 (6)	0.0374 (7)	0.0034 (5)	0.0054 (5)	0.0176 (6)
O3	0.0237 (6)	0.0306 (7)	0.0305 (7)	0.0067 (5)	0.0098 (5)	0.0168 (6)
O4	0.0547 (9)	0.0216 (6)	0.0254 (7)	-0.0050 (6)	0.0003 (6)	0.0128 (5)
N1	0.0232 (7)	0.0164 (6)	0.0187 (6)	-0.0006 (5)	0.0042 (5)	0.0053 (5)
N2	0.0527 (11)	0.0158 (7)	0.0227 (8)	-0.0083 (7)	0.0013 (7)	0.0061 (6)
C8	0.0212 (8)	0.0164 (7)	0.0216 (8)	-0.0002 (6)	0.0054 (6)	0.0087 (6)
C7	0.0207 (7)	0.0133 (7)	0.0174 (7)	-0.0012 (6)	0.0067 (6)	0.0046 (6)
C4	0.0210 (8)	0.0157 (7)	0.0212 (8)	0.0005 (6)	0.0050 (6)	0.0065 (6)
C5	0.0242 (8)	0.0168 (7)	0.0190 (7)	0.0013 (6)	0.0053 (6)	0.0071 (6)

C3	0.0363 (10)	0.0205 (8)	0.0187 (8)	-0.0043 (7)	0.0021 (7)	0.0057 (7)
C6	0.0269 (8)	0.0157 (7)	0.0226 (8)	0.0013 (6)	0.0037 (6)	0.0073 (6)
C1	0.0309 (9)	0.0168 (8)	0.0252 (9)	-0.0037 (7)	0.0050 (7)	0.0086 (7)
C2	0.0454 (11)	0.0240 (9)	0.0218 (9)	-0.0038 (8)	0.0045 (8)	0.0125 (7)

*Geometric parameters (Å, °)*

Ni1—O2 <sup>i</sup>	2.0484 (12)	N2—H2A	0.8600
Ni1—O2	2.0484 (12)	N2—H2B	0.8600
Ni1—O3	2.0792 (13)	C8—C8 <sup>ii</sup>	1.326 (3)
Ni1—O3 <sup>i</sup>	2.0792 (13)	C8—C7	1.500 (2)
Ni1—N1	2.1187 (14)	C8—H8	0.9300
Ni1—N1 <sup>i</sup>	2.1187 (14)	C4—C5	1.386 (2)
O2—C7	1.266 (2)	C4—C3	1.388 (2)
O1—C7	1.248 (2)	C4—C6	1.500 (2)
O3—H3A	0.8501	C5—H5	0.9300
O3—H3B	0.8501	C3—C2	1.387 (3)
O4—C6	1.236 (2)	C3—H3	0.9300
N1—C1	1.340 (2)	C1—C2	1.379 (3)
N1—C5	1.341 (2)	C1—H1	0.9300
N2—C6	1.327 (2)	C2—H2	0.9300
O2 <sup>i</sup> —Ni1—O2	180.0	C8 <sup>ii</sup> —C8—C7	124.0 (2)
O2 <sup>i</sup> —Ni1—O3	96.22 (5)	C8 <sup>ii</sup> —C8—H8	118.0
O2—Ni1—O3	83.78 (5)	C7—C8—H8	118.0
O2 <sup>i</sup> —Ni1—O3 <sup>i</sup>	83.78 (5)	O1—C7—O2	126.09 (15)
O2—Ni1—O3 <sup>i</sup>	96.22 (5)	O1—C7—C8	119.43 (14)
O3—Ni1—O3 <sup>i</sup>	180.0	O2—C7—C8	114.47 (14)
O2 <sup>i</sup> —Ni1—N1	89.41 (5)	C5—C4—C3	118.21 (15)
O2—Ni1—N1	90.59 (5)	C5—C4—C6	117.84 (15)
O3—Ni1—N1	86.92 (5)	C3—C4—C6	123.89 (15)
O3 <sup>i</sup> —Ni1—N1	93.08 (5)	N1—C5—C4	123.40 (15)
O2 <sup>i</sup> —Ni1—N1 <sup>i</sup>	90.59 (5)	N1—C5—H5	118.3
O2—Ni1—N1 <sup>i</sup>	89.41 (5)	C4—C5—H5	118.3
O3—Ni1—N1 <sup>i</sup>	93.08 (5)	C2—C3—C4	118.71 (16)
O3 <sup>i</sup> —Ni1—N1 <sup>i</sup>	86.92 (5)	C2—C3—H3	120.6
N1—Ni1—N1 <sup>i</sup>	180.00 (8)	C4—C3—H3	120.6
C7—O2—Ni1	128.31 (11)	O4—C6—N2	122.05 (16)
Ni1—O3—H3A	109.5	O4—C6—C4	120.06 (16)
Ni1—O3—H3B	109.3	N2—C6—C4	117.87 (15)
H3A—O3—H3B	109.5	N1—C1—C2	122.83 (16)
C1—N1—C5	117.63 (15)	N1—C1—H1	118.6
C1—N1—Ni1	120.90 (11)	C2—C1—H1	118.6
C5—N1—Ni1	121.25 (11)	C1—C2—C3	119.17 (17)
C6—N2—H2A	120.0	C1—C2—H2	120.4
C6—N2—H2B	120.0	C3—C2—H2	120.4
H2A—N2—H2B	120.0		

Ni1—O2—C7—O1	-26.7 (2)	C6—C4—C3—C2	176.66 (18)
Ni1—O2—C7—C8	151.80 (11)	C5—C4—C6—O4	-1.8 (3)
C8 <sup>ii</sup> —C8—C7—O1	-6.3 (3)	C3—C4—C6—O4	-178.95 (19)
C8 <sup>ii</sup> —C8—C7—O2	175.1 (2)	C5—C4—C6—N2	176.32 (17)
C1—N1—C5—C4	-2.4 (3)	C3—C4—C6—N2	-0.8 (3)
Ni1—N1—C5—C4	172.22 (13)	C5—N1—C1—C2	0.3 (3)
C3—C4—C5—N1	2.5 (3)	Ni1—N1—C1—C2	-174.31 (16)
C6—C4—C5—N1	-174.83 (15)	N1—C1—C2—C3	1.5 (3)
C5—C4—C3—C2	-0.5 (3)	C4—C3—C2—C1	-1.4 (3)

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3A $\cdots$ O4 <sup>iii</sup>	0.85	2.06	2.8699 (19)	159
O3—H3B $\cdots$ O1 <sup>iv</sup>	0.85	2.17	2.8550 (19)	138
O3—H3B $\cdots$ O1 <sup>i</sup>	0.85	2.30	2.9916 (18)	138
N2—H2A $\cdots$ O4 <sup>v</sup>	0.86	2.16	2.980 (2)	158
N2—H2B $\cdots$ O1 <sup>vi</sup>	0.86	2.10	2.929 (2)	161
C3—H3 $\cdots$ O1 <sup>vi</sup>	0.93	2.40	3.296 (2)	162

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