

## Diaquabis(2-chlorobenzoato- $\kappa$ O)-bis(nicotinamide- $\kappa$ N<sup>1</sup>)nickel(II)

Tuncer Hökelek,<sup>a\*</sup> Hakan Dal,<sup>b</sup> Barış Tercan,<sup>c</sup> F. Elif Özbek<sup>d</sup> and Hacali Necefoğlu<sup>d</sup>

<sup>a</sup>Hacettepe University, Department of Physics, 06800 Beytepe, Ankara, Turkey,

<sup>b</sup>Anadolu University, Faculty of Science, Department of Chemistry, 26470

Yenişehir, Eskişehir, Turkey, <sup>c</sup>Karabük University, Department of Physics, 78050,

Karabük, Turkey, and <sup>d</sup>Kafkas University, Department of Chemistry, 63100 Kars,

Turkey

Correspondence e-mail: merzifon@hacettepe.edu.tr

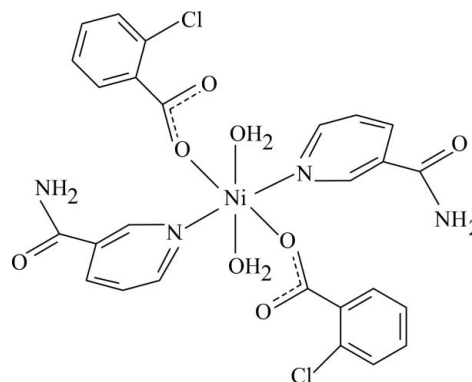
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.040;  $wR$  factor = 0.107; data-to-parameter ratio = 16.3.

The title Ni<sup>II</sup> complex,  $[\text{Ni}(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$ , is centrosymmetric with the Ni atom located on an inversion centre. The molecule contains two 2-chlorobenzoate (CB) and two nicotinamide (NA) ligands and two water molecules, all ligands being monodentate. The four O atoms in the equatorial plane around the Ni atom form a slightly distorted square-planar arrangement, while the slightly distorted octahedral coordination is completed by the two N atoms of the NA ligands in the axial positions. The dihedral angle between the carboxyl group and the adjacent benzene ring is  $29.48(16)^\circ$ , while the pyridine and benzene rings are oriented at a dihedral angle of  $83.16(5)^\circ$ . In the crystal structure, O—H...O and N—H...O hydrogen bonds link the molecules into infinite chains.  $\pi$ — $\pi$  Contacts between the benzene and pyridine rings [centroid—centroid distance =  $3.952(1)$  Å] may further stabilize the crystal structure. There is also a C—H... $\pi$  interaction.

### Related literature

For general background, see: Antolini *et al.* (1982); Bigoli *et al.* (1972); Krishnamachari (1974); Nadzhafov *et al.* (1981); Shnulin *et al.* (1981). For related structures, see: Hökelek & Necefoğlu (1996, 1997, 2007); Hökelek *et al.* (1995, 1997, 2007, 2008); Özbek *et al.* (2009); Sertçelik *et al.* (2009a,b,c); Tercan *et al.* (2009).



### Experimental

#### Crystal data

$[\text{Ni}(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$

$M_r = 650.10$

Monoclinic,  $P2_1/n$

$a = 7.8602(3)$  Å

$b = 17.9529(6)$  Å

$c = 9.8446(3)$  Å

$\beta = 106.600(2)^\circ$

$V = 1331.31(8)$  Å<sup>3</sup>

$Z = 2$

Mo  $K\alpha$  radiation

$\mu = 0.99$  mm<sup>-1</sup>

$T = 100$  K

$0.45 \times 0.30 \times 0.25$  mm

#### Data collection

Bruker Kappa-APEXII CCD

area-detector diffractometer

Absorption correction: multi-scan

(*SADABS*; Bruker, 2005)

$T_{\min} = 0.710$ ,  $T_{\max} = 0.784$

11754 measured reflections

3301 independent reflections

2626 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.064$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.107$

$S = 1.07$

3301 reflections

202 parameters

1 restraint

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.77$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.69$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ni1—O1	2.1017 (16)	Ni1—N1	2.1217 (18)
Ni1—O4	2.1520 (16)		

**Table 2**

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>
O4—H41...O2	0.84 (4)	1.82 (3)	2.630 (2)	161 (3)
O4—H42...O3 <sup>ii</sup>	0.85 (3)	2.09 (3)	2.887 (2)	156 (3)
N2—H21...O2 <sup>iii</sup>	0.79 (3)	2.13 (3)	2.865 (3)	156 (3)
N2—H22...O3 <sup>iv</sup>	0.84 (3)	2.16 (3)	2.934 (3)	153 (3)
C9—H9...Cg1 <sup>iii</sup>	0.93	2.88	3.596 (2)	135

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for

publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2501).

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**supplementary materials**

*Acta Cryst.* (2009). E65, m466-m467 [ doi:10.1107/S1600536809011209 ]

## Diaquabis(2-chlorobenzoato- $\kappa O$ )bis(nicotinamide- $\kappa N^1$ )nickel(II)

T. Hökelek, H. Dal, B. Tercan, F. E. Özbek and H. Necefoglu

### Comment

Transition metal complexes with biochemically active ligands frequently show interesting physical and/or chemical properties, as a result they may find applications in biological systems (Antolini *et al.*, 1982). The structural functions and coordination relationships of the arylcarboxylate ion in transition metal complexes of benzoic acid derivatives change depending on the nature and position of the substituent groups on the benzene ring, the nature of the additional ligand molecule or solvent, and the medium of the synthesis (Nadzhafov *et al.*, 1981; Shnulin *et al.*, 1981). Nicotinamide (NA) is one form of niacin and a deficiency of this vitamin leads to loss of copper from the body, known as pellagra disease. Victims of pellagra show unusually high serum and urinary copper levels (Krishnamachari, 1974). On the other hand, the nicotinic acid derivative *N,N*-diethylnicotinamide (DENA) is an important respiratory stimulant (Bigoli *et al.*, 1972).

The structure determination of the title compound, (I), a nickel complex with two 2-chlorobenzoate (CB), two nicotinamide (NA) ligands and two water molecules, was undertaken in order to determine the properties of the ligands and also to compare the results obtained with those reported previously.

Compound (I) is a monomeric complex, with the Ni atom on a centre of symmetry. It contains two CB, two NA ligands and two water molecules (Fig. 1). All ligands are monodentate. The four O atoms (O1, O4, and the symmetry-related atoms, O1', O4') in the equatorial plane around the Ni atom form a slightly distorted square-planar arrangement, while the slightly distorted octahedral coordination is completed by the two N atoms of the NA ligands (N1, N1') in the axial positions (Table 1 and Fig. 1). The intramolecular O—H $\cdots$ O hydrogen bonds (Table 2) link two of the water molecules to the two CB ligands (Fig. 1).

The near equality of the C1—O1 [1.267 (3) Å] and C1—O2 [1.258 (3) Å] bonds in the carboxylate group indicates a delocalized bonding arrangement, rather than localized single and double bonds, and may be compared with the corresponding distances: 1.262 (3) and 1.249 (3) Å in [Mn(DENA)<sub>2</sub>(C<sub>8</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], (II) (Sertçelik *et al.*, 2009a), 1.263 (4) and 1.249 (4) Å in [Ni(DENA)<sub>2</sub>(C<sub>8</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], (III) (Sertçelik *et al.*, 2009b), 1.262 (5) and 1.257 (5) Å in [Co(DENA)<sub>2</sub>(C<sub>8</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], (IV) (Sertçelik *et al.*, 2009c), 1.244 (4) and 1.270 (4) Å in [Co(NA)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>](C<sub>7</sub>H<sub>4</sub>FO<sub>2</sub>)<sub>2</sub>, (V) (Özbek *et al.*, 2009), 1.284 (2), 1.248 (2) and 1.278 (2), 1.241 (2) Å in [Zn(NA)<sub>2</sub>(C<sub>8</sub>H<sub>8</sub>NO<sub>2</sub>)<sub>2</sub>], (VI) (Tercan *et al.*, 2009), 1.256 (6) and 1.245 (6) Å in [Mn(DENA)<sub>2</sub>(C<sub>7</sub>H<sub>4</sub>ClO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], (VII) (Hökelek *et al.*, 2008), 1.265 (6) and 1.275 (6) Å in [Mn(C<sub>9</sub>H<sub>10</sub>NO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>].2(H<sub>2</sub>O), (VIII) (Hökelek & Necefoglu, 2007), 1.260 (4) and 1.252 (4) Å in [Zn(DENA)<sub>2</sub>(C<sub>7</sub>H<sub>4</sub>FO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], (IX) (Hökelek *et al.*, 2007), 1.259 (9) and 1.273 (9) Å in Cu<sub>2</sub>(DENA)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>COO)<sub>4</sub>, (X) (Hökelek *et al.*, 1995), 1.279 (4) and 1.246 (4) Å in [Zn<sub>2</sub>(DENA)<sub>2</sub>(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>4</sub>].2H<sub>2</sub>O, (XI) (Hökelek & Necefoglu, 1996), 1.251 (6) and 1.254 (7) Å in [Co(DENA)<sub>2</sub>(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], (XII) (Hökelek & Necefoglu, 1997) and 1.278 (3) and 1.246 (3) Å in [Cu(DENA)<sub>2</sub>(C<sub>7</sub>H<sub>4</sub>NO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], (XIII) (Hökelek *et al.*, 1997). In (I), the average Ni—O bond length is 2.1269 (16) Å and the Ni atom is displaced out of the least-squares plane of the carboxylate group (O1/C1/O2) by 0.661 (1) Å. The dihedral angle between the planar carboxylate group and the benzene ring A (C2—C7) is 29.48 (16)°, while that between rings A and B (N1/C8—C12) is 83.16 (5)°.

## supplementary materials

In the crystal structure, intermolecular O—H $\cdots$ O and N—H $\cdots$ O hydrogen bonds (Table 2) link the molecules into infinite chains (Fig. 2), in which they may be effective in the stabilization of the structure. The  $\pi$ - $\pi$  contacts between the 2-chlorobenzoate rings and the pyridine rings of NA ligands, Cg2—Cg1<sup>1</sup> [symmetry code: (i)  $x - 1/2, 1/2 - y, 1/2 + z$ , where Cg1 and Cg2 are centroids of the rings A (C2—C7) and B (N1/C9—C13), respectively] may further stabilize the structure, with centroid-centroid distance of 3.952 (1) Å. There is also a C—H $\cdots$  $\pi$  interaction (Table 2).

### Experimental

The title compound was prepared by the reaction of Ni(SO<sub>4</sub>).6(H<sub>2</sub>O) (1.31 g, 5 mmol) in H<sub>2</sub>O (20 ml) and NA (1.22 g, 10 mmol) in H<sub>2</sub>O (20 ml) with sodium 2-chlorobenzoate (1.785 g, 10 mmol) in H<sub>2</sub>O (50 ml). The mixture was filtered and set aside to crystallize at ambient temperature for 5 d, giving orange single crystals.

### Refinement

H atoms of water molecule and NH<sub>2</sub> group were located in difference Fourier maps and refined isotropically, with restraint of O4—H42 = 0.850 (18) Å. The remaining H atoms were positioned geometrically with C—H = 0.93 Å, for aromatic H atoms and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

### Figures

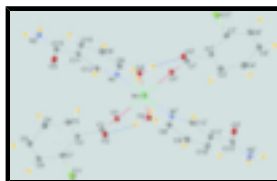


Fig. 1. The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. Primed atoms are generated by the symmetry operator (1 -  $x$ , - $y$ , - $z$ ).

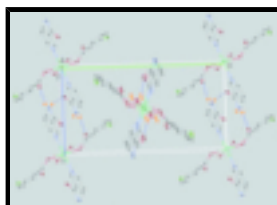


Fig. 2. A partial packing diagram of (I) viewed down the  $a$  axis, showing hydrogen bonds (dotted lines) linking the molecules into chains, where  $b$  and  $c$  axes are horizontal and vertical, respectively. H atoms not involved in hydrogen bonding are omitted.

### Diaquabis(2-chlorobenzoato- $\kappa$ O)bis(nicotinamide- $\kappa$ N<sup>1</sup>)nickel(II)

#### Crystal data

[Ni(C<sub>7</sub>H<sub>4</sub>ClO<sub>2</sub>)<sub>2</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>]

$M_r = 650.10$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 7.8602$  (3) Å

$b = 17.9529$  (6) Å

$c = 9.8446$  (3) Å

$F_{000} = 668$

$D_x = 1.622$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 5500 reflections

$\theta = 2.4$ – $28.3^\circ$

$\mu = 0.99$  mm<sup>-1</sup>

$T = 100$  K

$\beta = 106.600 (2)^\circ$  Block, orange  
 $V = 1331.31 (8) \text{ \AA}^3$   $0.45 \times 0.30 \times 0.25 \text{ mm}$   
 $Z = 2$

*Data collection*

Bruker Kappa-APEXII CCD area-detector diffractometer	3301 independent reflections
Radiation source: fine-focus sealed tube	2626 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.064$
$T = 100 \text{ K}$	$\theta_{\text{max}} = 28.3^\circ$
$\varphi$ and $\omega$ scans	$\theta_{\text{min}} = 2.3^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$h = -10 \rightarrow 7$
$T_{\text{min}} = 0.710, T_{\text{max}} = 0.784$	$k = -23 \rightarrow 21$
11754 measured reflections	$l = -11 \rightarrow 13$

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.107$	$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 1.0761P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
3301 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
202 parameters	$\Delta\rho_{\text{max}} = 0.77 \text{ e \AA}^{-3}$
1 restraint	$\Delta\rho_{\text{min}} = -0.69 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

*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 ( $\text{Å}^2$ )*

$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
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## supplementary materials

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Ni1	0.5000	0.0000	0.0000	0.01322 (13)
Cl1	0.40816 (8)	0.28820 (3)	-0.32584 (6)	0.02186 (16)
O1	0.6153 (2)	0.09893 (9)	-0.04613 (15)	0.0135 (3)
O2	0.3868 (2)	0.13652 (10)	-0.22542 (16)	0.0155 (4)
O3	0.0484 (2)	0.00967 (10)	0.32471 (17)	0.0183 (4)
O4	0.2363 (2)	0.04330 (10)	-0.08886 (17)	0.0146 (4)
H41	0.261 (4)	0.0763 (19)	-0.141 (3)	0.030 (9)*
H42	0.153 (3)	0.0172 (16)	-0.141 (3)	0.029*
N1	0.4964 (3)	0.04416 (10)	0.19906 (19)	0.0115 (4)
N2	0.1426 (3)	0.08165 (13)	0.5195 (2)	0.0188 (5)
H21	0.221 (4)	0.1030 (18)	0.573 (3)	0.026 (9)*
H22	0.060 (4)	0.0657 (17)	0.550 (3)	0.023 (8)*
C1	0.5480 (3)	0.13795 (13)	-0.1555 (2)	0.0121 (4)
C2	0.6718 (3)	0.18573 (13)	-0.2104 (2)	0.0124 (5)
C3	0.8477 (3)	0.16293 (13)	-0.1863 (2)	0.0143 (5)
H3	0.8887	0.1224	-0.1271	0.017*
C4	0.9630 (3)	0.19869 (14)	-0.2478 (2)	0.0164 (5)
H4	1.0797	0.1824	-0.2294	0.020*
C5	0.9033 (3)	0.25927 (14)	-0.3375 (2)	0.0166 (5)
H5	0.9789	0.2823	-0.3820	0.020*
C6	0.7319 (3)	0.28498 (14)	-0.3601 (2)	0.0154 (5)
H6	0.6926	0.3262	-0.4179	0.019*
C7	0.6181 (3)	0.24896 (13)	-0.2959 (2)	0.0129 (5)
C8	0.6344 (3)	0.08184 (13)	0.2847 (2)	0.0132 (5)
H8	0.7379	0.0868	0.2577	0.016*
C9	0.6273 (3)	0.11327 (14)	0.4113 (2)	0.0169 (5)
H9	0.7240	0.1393	0.4678	0.020*
C10	0.4743 (3)	0.10541 (13)	0.4526 (2)	0.0152 (5)
H10	0.4668	0.1262	0.5372	0.018*
C11	0.3318 (3)	0.06602 (13)	0.3664 (2)	0.0123 (4)
C12	0.3496 (3)	0.03681 (13)	0.2405 (2)	0.0125 (5)
H12	0.2543	0.0108	0.1819	0.015*
C13	0.1630 (3)	0.05107 (13)	0.4022 (2)	0.0142 (5)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.0129 (2)	0.0162 (2)	0.00877 (19)	-0.00046 (17)	0.00017 (15)	-0.00017 (15)
Cl1	0.0173 (3)	0.0200 (3)	0.0261 (3)	0.0068 (2)	0.0027 (2)	0.0055 (2)
O1	0.0147 (8)	0.0153 (8)	0.0076 (7)	-0.0023 (6)	-0.0017 (6)	0.0006 (6)
O2	0.0117 (8)	0.0213 (9)	0.0109 (7)	-0.0014 (7)	-0.0013 (6)	0.0023 (6)
O3	0.0149 (9)	0.0267 (10)	0.0116 (7)	-0.0053 (7)	0.0013 (6)	-0.0039 (7)
O4	0.0134 (9)	0.0176 (9)	0.0103 (7)	-0.0009 (7)	-0.0006 (6)	0.0013 (6)
N1	0.0115 (9)	0.0122 (10)	0.0090 (8)	0.0000 (7)	-0.0002 (7)	0.0004 (7)
N2	0.0157 (11)	0.0294 (13)	0.0116 (9)	-0.0060 (9)	0.0043 (8)	-0.0067 (9)
C1	0.0148 (11)	0.0124 (11)	0.0082 (9)	-0.0007 (9)	0.0018 (8)	-0.0030 (8)
C2	0.0154 (11)	0.0129 (11)	0.0072 (9)	-0.0011 (9)	0.0004 (8)	-0.0023 (8)
C3	0.0147 (11)	0.0137 (11)	0.0112 (10)	-0.0007 (9)	-0.0016 (8)	-0.0014 (8)

C4	0.0133 (11)	0.0187 (12)	0.0157 (11)	-0.0020 (9)	0.0016 (9)	-0.0026 (9)
C5	0.0190 (12)	0.0174 (12)	0.0127 (10)	-0.0053 (10)	0.0035 (9)	-0.0016 (9)
C6	0.0189 (12)	0.0145 (12)	0.0099 (10)	-0.0022 (9)	-0.0007 (8)	0.0008 (8)
C7	0.0126 (11)	0.0140 (11)	0.0092 (10)	0.0017 (9)	-0.0013 (8)	-0.0020 (8)
C8	0.0120 (11)	0.0154 (12)	0.0109 (10)	-0.0009 (9)	0.0010 (8)	0.0006 (8)
C9	0.0155 (12)	0.0196 (13)	0.0125 (10)	-0.0047 (10)	-0.0012 (9)	-0.0033 (9)
C10	0.0177 (12)	0.0188 (12)	0.0071 (9)	-0.0023 (9)	0.0005 (8)	-0.0028 (8)
C11	0.0134 (11)	0.0134 (11)	0.0082 (9)	-0.0007 (9)	-0.0001 (8)	0.0007 (8)
C12	0.0131 (11)	0.0123 (11)	0.0091 (9)	-0.0006 (9)	-0.0018 (8)	0.0011 (8)
C13	0.0132 (11)	0.0180 (12)	0.0097 (9)	0.0004 (9)	0.0008 (8)	0.0017 (8)

*Geometric parameters (Å, °)*

Ni1—O1 <sup>i</sup>	2.1017 (16)	C3—H3	0.9300
Ni1—O1	2.1017 (16)	C4—C3	1.383 (3)
Ni1—O4	2.1520 (16)	C4—C5	1.395 (3)
Ni1—O4 <sup>i</sup>	2.1520 (16)	C4—H4	0.9300
Ni1—N1 <sup>i</sup>	2.1217 (18)	C5—C6	1.381 (3)
Ni1—N1	2.1217 (18)	C5—H5	0.9300
C11—C7	1.740 (2)	C6—H6	0.9300
O1—C1	1.267 (3)	C7—C2	1.404 (3)
O2—C1	1.258 (3)	C7—C6	1.393 (3)
O3—C13	1.246 (3)	C8—C9	1.384 (3)
O4—H41	0.85 (3)	C8—H8	0.9300
O4—H42	0.850 (18)	C9—H9	0.9300
N1—C8	1.350 (3)	C10—C9	1.382 (3)
N1—C12	1.335 (3)	C10—H10	0.9300
N2—C13	1.329 (3)	C11—C10	1.390 (3)
N2—H21	0.79 (3)	C11—C12	1.389 (3)
N2—H22	0.84 (3)	C11—C13	1.492 (3)
C1—C2	1.508 (3)	C12—H12	0.9300
C2—C3	1.396 (3)		
O1 <sup>i</sup> —Ni1—O1	180.00 (5)	C4—C3—C2	122.0 (2)
O1 <sup>i</sup> —Ni1—O4	88.18 (6)	C4—C3—H3	119.0
O1—Ni1—O4	91.82 (6)	C3—C4—C5	119.7 (2)
O1 <sup>i</sup> —Ni1—O4 <sup>i</sup>	91.82 (6)	C3—C4—H4	120.2
O1—Ni1—O4 <sup>i</sup>	88.18 (6)	C5—C4—H4	120.2
O4—Ni1—O4 <sup>i</sup>	180.00 (9)	C4—C5—H5	120.1
O1 <sup>i</sup> —Ni1—N1 <sup>i</sup>	90.24 (7)	C6—C5—C4	119.9 (2)
O1—Ni1—N1 <sup>i</sup>	89.76 (7)	C6—C5—H5	120.1
O1 <sup>i</sup> —Ni1—N1	89.76 (7)	C5—C6—C7	119.7 (2)
O1—Ni1—N1	90.24 (7)	C5—C6—H6	120.2
N1 <sup>i</sup> —Ni1—N1	180.00 (14)	C7—C6—H6	120.2
N1 <sup>i</sup> —Ni1—O4	91.44 (7)	C2—C7—C11	122.46 (19)
N1—Ni1—O4	88.56 (7)	C6—C7—C11	115.85 (18)
N1 <sup>i</sup> —Ni1—O4 <sup>i</sup>	88.56 (7)	C6—C7—C2	121.7 (2)



## supplementary materials

N1—Ni1—O4 <sup>i</sup>	91.44 (7)	N1—C8—C9	122.3 (2)
Ni1—O4—H41	98 (2)	N1—C8—H8	118.8
Ni1—O4—H42	122 (2)	C9—C8—H8	118.8
H41—O4—H42	107 (3)	C8—C9—H9	120.5
C1—O1—Ni1	123.37 (14)	C10—C9—C8	119.1 (2)
C8—N1—Ni1	122.93 (16)	C10—C9—H9	120.5
C12—N1—Ni1	119.06 (14)	C9—C10—C11	119.3 (2)
C12—N1—C8	117.97 (19)	C9—C10—H10	120.4
C13—N2—H21	121 (2)	C11—C10—H10	120.4
C13—N2—H22	118 (2)	C10—C11—C13	124.3 (2)
H22—N2—H21	118 (3)	C12—C11—C10	117.9 (2)
O1—C1—C2	117.6 (2)	C12—C11—C13	117.80 (19)
O2—C1—O1	124.4 (2)	N1—C12—C11	123.4 (2)
O2—C1—C2	117.89 (19)	N1—C12—H12	118.3
C3—C2—C1	118.8 (2)	C11—C12—H12	118.3
C3—C2—C7	116.9 (2)	O3—C13—N2	122.2 (2)
C7—C2—C1	124.1 (2)	O3—C13—C11	119.9 (2)
C2—C3—H3	119.0	N2—C13—C11	117.9 (2)
O4—Ni1—O1—C1	-35.17 (18)	C1—C2—C3—C4	172.0 (2)
O4 <sup>i</sup> —Ni1—O1—C1	144.83 (18)	C7—C2—C3—C4	-2.5 (3)
N1 <sup>i</sup> —Ni1—O1—C1	56.26 (18)	C5—C4—C3—C2	-0.3 (3)
N1—Ni1—O1—C1	-123.74 (18)	C3—C4—C5—C6	2.5 (3)
O1 <sup>i</sup> —Ni1—N1—C8	136.61 (18)	C4—C5—C6—C7	-1.7 (3)
O1—Ni1—N1—C8	-43.39 (18)	C11—C7—C2—C1	10.4 (3)
O1 <sup>i</sup> —Ni1—N1—C12	-45.66 (17)	C11—C7—C2—C3	-175.42 (16)
O1—Ni1—N1—C12	134.34 (17)	C6—C7—C2—C1	-170.8 (2)
O4—Ni1—N1—C12	42.53 (17)	C6—C7—C2—C3	3.4 (3)
O4 <sup>i</sup> —Ni1—N1—C12	-137.47 (17)	C11—C7—C6—C5	177.53 (17)
O4—Ni1—N1—C8	-135.20 (18)	C2—C7—C6—C5	-1.3 (3)
O4 <sup>i</sup> —Ni1—N1—C8	44.80 (18)	N1—C8—C9—C10	0.6 (4)
Ni1—O1—C1—O2	22.1 (3)	C11—C10—C9—C8	0.2 (4)
Ni1—O1—C1—C2	-154.02 (15)	C12—C11—C10—C9	-0.7 (3)
Ni1—N1—C8—C9	176.99 (17)	C13—C11—C10—C9	177.3 (2)
C12—N1—C8—C9	-0.8 (3)	C10—C11—C12—N1	0.5 (3)
Ni1—N1—C12—C11	-177.65 (17)	C13—C11—C12—N1	-177.6 (2)
C8—N1—C12—C11	0.2 (3)	C10—C11—C13—O3	-173.6 (2)
O1—C1—C2—C3	28.5 (3)	C10—C11—C13—N2	4.8 (4)
O1—C1—C2—C7	-157.4 (2)	C12—C11—C13—O3	4.4 (3)
O2—C1—C2—C3	-147.9 (2)	C12—C11—C13—N2	-177.1 (2)
O2—C1—C2—C7	26.2 (3)		

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

### Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O4—H41 $\cdots$ O2	0.84 (4)	1.82 (3)	2.630 (2)	161 (3)
O4—H42 $\cdots$ O3 <sup>ii</sup>	0.85 (3)	2.09 (3)	2.887 (2)	156 (3)

N2—H21...O2 <sup>iii</sup>	0.79 (3)	2.13 (3)	2.865 (3)	156 (3)
N2—H22...O3 <sup>iv</sup>	0.84 (3)	2.16 (3)	2.934 (3)	153 (3)
C9—H9...Cg1 <sup>iii</sup>	0.93	2.88	3.596 (2)	135

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

Fig. 1

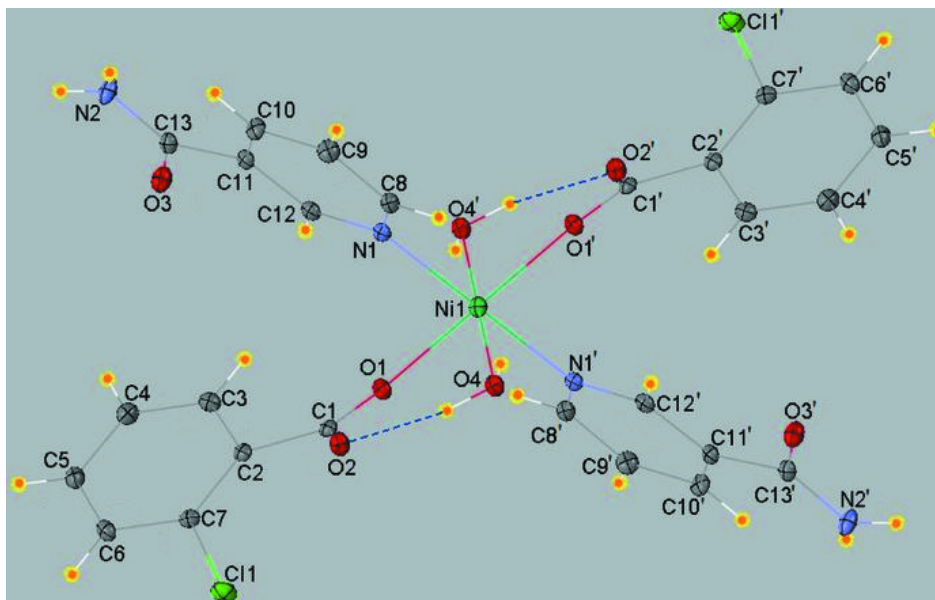


Fig. 2

