

Crystal structure and Hirshfeld surface analysis of diaquabis(isonicotinamide- κN)bis(2,4,6-trimethylbenzoato- κO^1)nickel(II) dihydrate

Tuncer Hökelek,^{a*} Gizem Sertkaya,^a Ezgi Ay,^a Safiye Özkaya^b and Hacali Necefoğlu^c

Received 8 June 2017
Accepted 18 July 2017

Edited by A. M. Chippindale, University of Reading, England

Keywords: crystal structure; nickel(II); coordination compound; benzoic acid; nicotinamide.

CCDC reference: 1562879

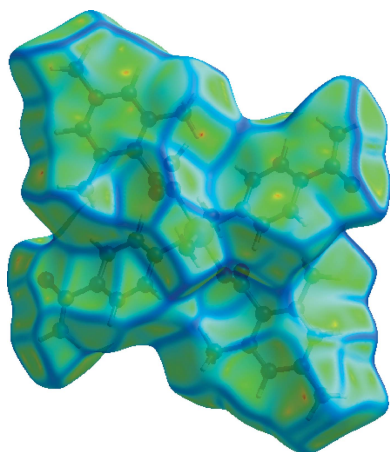
Supporting information: this article has supporting information at journals.iucr.org/e

^aDepartment of Physics, Hacettepe University, 06800 Beytepe, Ankara, Turkey, ^bDepartment of Chemistry, Kafkas University, 36100 Kars, Turkey, and ^cDepartment of Chemistry, Kafkas University, 36100 Kars, Turkey, International Scientific Research Centre, Baku State University, 1148 Baku, Azerbaijan. *Correspondence e-mail: merzifon@hacettepe.edu.tr

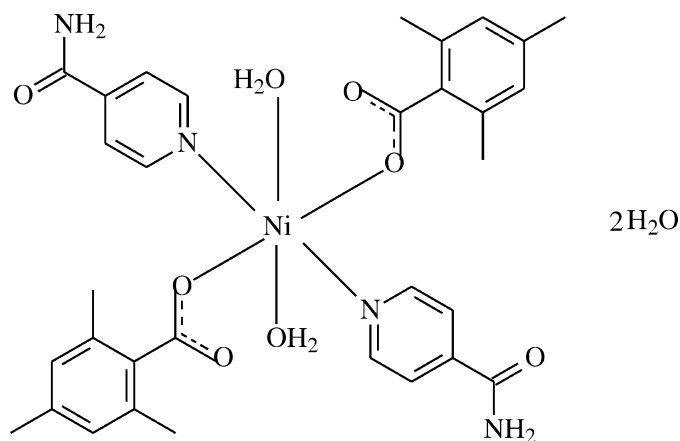
In the title Ni^{II} complex, [Ni(C₁₀H₁₁O₂)₂(C₆H₆N₂O)₂(H₂O)₂].2H₂O, the divalent Ni ion occupies a crystallographically imposed centre of symmetry and is coordinated by two O atoms from the carboxylate groups of two 2,4,6-trimethylbenzoate (TMB) ligands [Ni–O = 2.0438 (12) Å], two N atoms from the pyridyl groups of two isonicotinamide (INA) ligands [Ni–N = 2.1506 (15) Å] and two water molecules [Ni–O = 2.0438 (12) Å] in a slightly distorted octahedral geometry. The coordinating water molecules are hydrogen bonded to the non-coordinating carboxylate O atom of the TMB ligand [O··O = 2.593 (3) Å], enclosing an *S*(6) hydrogen-bonding motif. Two solvent water molecules are also present in the formula unit. In the crystal, a network of intermolecular N–H··O and O–H··O hydrogen bonds link the complexes into a three-dimensional array. Hirshfeld surface analysis indicates that the most important contributions for the crystal packing are from H··H (59.8%), O··H/H··O (20.2%) and C··H/H··C (13.7%) interactions.

1. Chemical context

Nicotinamide (NA) is a derivative of nicotinic acid, also called niacin. A deficiency in this vitamin leads to loss of copper from the body, giving rise to a condition known as pellagra disease. Victims of pellagra show unusually high serum and urinary copper levels (Krishnamachari, 1974). The crystal structure of NA was first determined in 1954 (Wright & King, 1954). The NA ring is the reactive part of nicotinamide adenine dinucleotide (NAD) and its phosphate (NADP), which are the major electron carriers in many biological oxidation–reduction reactions (You *et al.*, 1978). Another nicotinic acid derivative, *N,N*-diethylnicotinamide (DENA), is an important respiratory stimulant (Bigoli *et al.*, 1972). Transition-metal complexes with ligands of biochemical interest, such as imidazole and some N-protected amino acids, often show interesting physical and/or chemical properties, which lead to applications in biological systems (Antolini *et al.*, 1982). There have been many reports of the crystal structures of metal complexes with benzoic acid derivatives, which are of interest because of the number of different coordination modes exhibited by the carboxylic acid groups. These include Co and Cd complexes with 4-aminobenzoic acid (Chen & Chen, 2002; Amiraslanov *et al.*, 1979; Hauptmann *et al.*, 2000), Co complexes with benzoic acid (Catterick *et al.*, 1974), 4-nitro-



benzoic acid (Nadzhafov *et al.*, 1981) and phthalic acid (Adiwidjaja *et al.*, 1978) and Cu complexes with 4-hydrochlorobenzoic acid (Shnulin *et al.*, 1981). Mn complexes closely related to the title compound have also been reported, *e.g.* diaquabis(4-nitrobenzoato)bis(1*H*-1,2,4-triazol-3-amine)-manganese(II) (Zhang *et al.*, 2013) and diaquabis(1*H*-imidazole)bis(4-nitrobenzoato)manganese(II) (Xu & Xu, 2004).



The crystal structures of anhydrous zinc(II) carboxylates are diverse and include one-dimensional (Guseinov *et al.*, 1984; Clegg *et al.*, 1986*a*), two-dimensional (Clegg *et al.*, 1986*b*, 1987) and three-dimensional (Capilla & Aranda, 1979) polymeric motifs of different types, while discrete monomeric complexes with octahedral or tetrahedral coordination geometry are found if water or other donor molecules are coordinated to Zn (van Niekerk *et al.*, 1953; Usabaliev *et al.*,

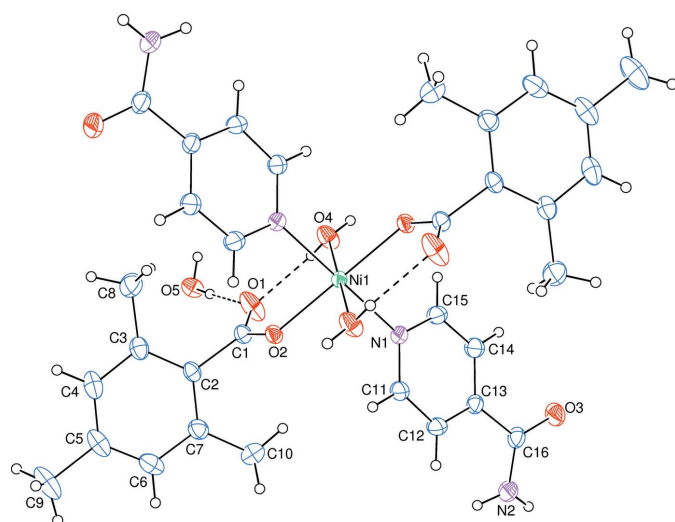


Figure 1
The molecular structure of the title complex with the atom-numbering scheme. Unlabelled atoms are related to corresponding labelled ones by the symmetry operation $(1 - x, -y, 1 - z)$. Displacement ellipsoids are drawn at the 50% probability level. $O-H_{\text{coordW}} \cdots O_c$ and $O-H_{\text{noncoordW}} \cdots O_c$ (c = carboxylate, coordW = coordinating water and noncoordW = non-coordinating water) hydrogen bonds are shown as dashed lines.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H21 \cdots O5^i$	0.84 (3)	2.18 (3)	3.014 (3)	174 (2)
$N2-H22 \cdots O3^{ii}$	0.83 (3)	2.21 (3)	3.043 (3)	177 (2)
$O4-H41 \cdots O5^{iii}$	0.77 (3)	2.02 (3)	2.745 (2)	157 (3)
$O4-H42 \cdots O1$	0.81 (3)	1.85 (3)	2.593 (3)	151 (3)
$O5-H51 \cdots O2^{iv}$	0.81 (3)	2.16 (3)	2.8804 (19)	148 (3)
$O5-H52 \cdots O1$	0.85 (3)	1.83 (3)	2.673 (2)	176 (2)
$C12-H12 \cdots O5^i$	0.93	2.56	3.307 (2)	137

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

1992). Pertinent to the present work, the structure–function–coordination relationships of the arylcarboxylate ion in Zn^{II} complexes of benzoic acid derivatives have been studied and shown to depend on the nature and position of the substituted groups on the benzene ring, the nature of the additional ligand, molecule or solvent, and the pH and temperature of synthesis (Shnulin *et al.*, 1981; Nadzhafov *et al.*, 1981; Antsyshkina *et al.*, 1980; Adiwidjaja *et al.*, 1978; Catterick *et al.*, 1974).

The structures of a number of mononuclear complexes of divalent transition-metal ions with both nicotinamide (NA) and benzoic acid derivatives as ligands have been previously reported and include $[Ni(C_7H_4ClO_2)_2(C_6H_6N_2O)_2(H_2O)_2]$ [(II); Hökelek *et al.*, 2009], $[Ni(C_8H_7O_2)_2(C_6H_6N_2O)_2(H_2O)_2]$ [(III); Necefoglu *et al.*, 2010], $[Ni(C_8H_7O_3)_2(C_6H_6N_2O)_2 \cdot 2(H_2O)]$ [(IV); Hökelek *et al.*, 2010], $[Ni(C_8H_5O_3)_2(C_6H_6N_2O)_2(H_2O)_2]$ [(V); Sertçelik *et al.*, 2012], $[Mn(C_7H_4NO_4)_2(C_6H_6N_2O)_2(H_2O)_2]$ [(VI); Aşkın *et al.*, 2016] and $[Zn(C_8H_8NO_2)_2(C_6H_6N_2O)_2]$ [(VII); Tercan *et al.*, 2009]. In this work, to enable comparison with the above Ni^{II} compounds and develop structure–function–coordination relationships, we describe the synthesis of diaquabis(isonicotinamide- κN)bis(2,4,6-trimethylbenzoato- κO^1)nickel(II) dihydrate, $[Ni(C_{10}H_{11}O_2)_2(C_6H_6N_2O)_2(H_2O)_2] \cdot 2H_2O$, and report its molecular and crystal structures, along with a Hirshfeld surface analysis.

2. Structural commentary

The asymmetric unit of the mononuclear title compound (I) contains a Ni^{II} cation residing on a centre of symmetry, one 2,4,6-trimethylbenzoate (TMB) anion and one isonicotinamide (INA) anion, together with one coordinating and one non-coordinating water molecule. The TMB and INA ligands coordinate in a monodentate manner (Fig. 1). In the complex, the Ni1 atom is in a slightly distorted octahedral environment and is coordinated by two carboxylate O atoms (O2 and O2ⁱ) of the monodentate TMB anions, two coordinating water O atoms (O4 and O4ⁱ) and two pyridine N atoms (N1 and N1ⁱ) of the monodentate INA ligands at distances of 2.0438 (12), 2.0346 (14) and 2.1506 (15) \AA , respectively [symmetry code: (i) $1 - x, -y, 1 - z$] (Fig. 1). The non-coordinating oxygen atoms of the carboxylate groups interact with the coordinating and non-coordinating water molecules *via* short hydrogen

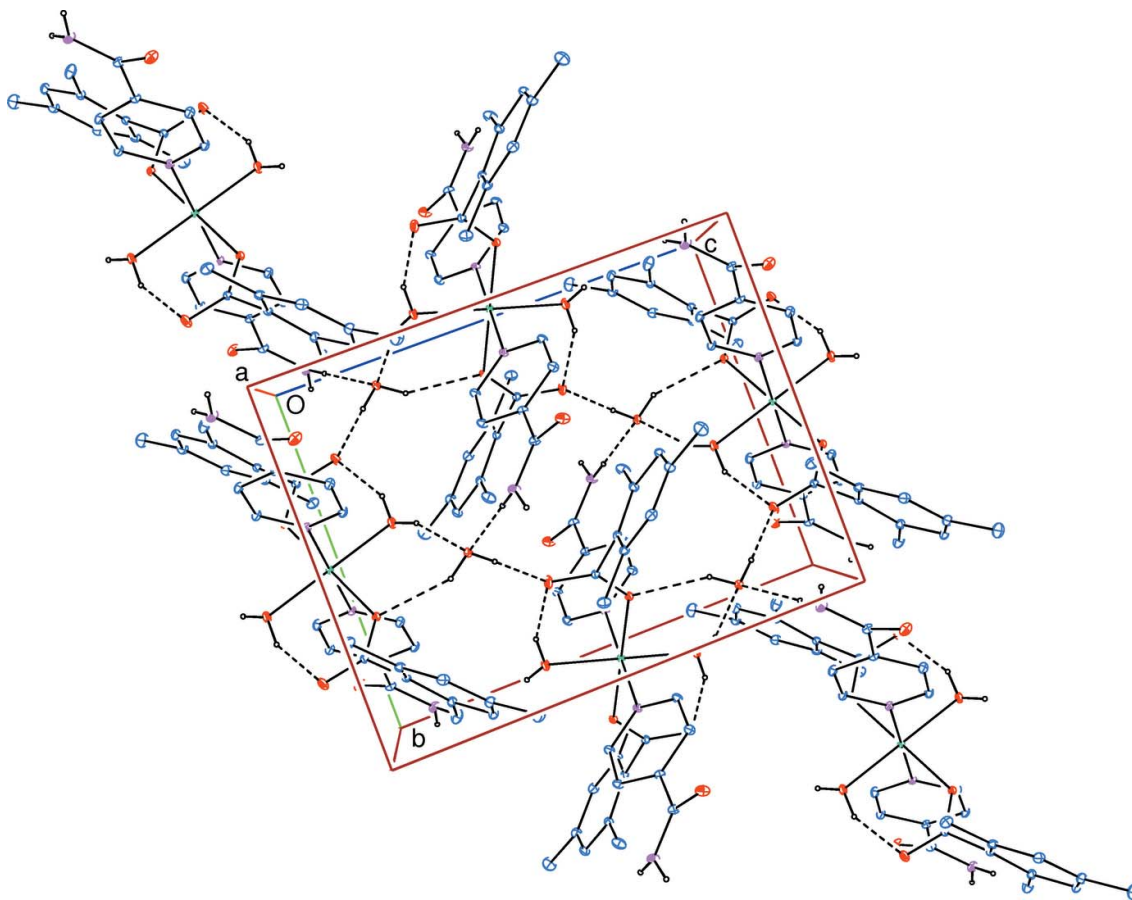


Figure 2

View of the hydrogen bonding and packing of the title complex along the *a* axis. Non-bonding H atoms have been omitted for clarity.

bonds (Table 1, Fig. 1). Intramolecular $O-H_{\text{coordW}} \cdots O_c$ (coordW = coordinating water and *c* = carboxylate) hydrogen bonds (Table 1) link H atoms of the coordinating water molecules to the non-coordinating carboxylate oxygen atoms, enclosing S(6) ring motifs (Fig. 1).

The near equalities of the C1–O1 [1.242 (2) Å] and C1–O2 [1.260 (2) Å] bonds in the carboxylate groups indicate delocalized bonding arrangements, rather than localized single and double bonds. The O2–C1–O1 bond angle [124.52 (17)°] is comparable the corresponding values of 124.4 (2)° in (II), 124.67 (14)° in (III), 124.22 (11)° in (IV), 125.71 (10)° in (V), 126.0 (3)° in (VI) and 120.47 (15) and 123.17 (15)° in (VII), where the benzoate ions also coordinate the metal atoms monodentately. The Ni1 atom lies 0.3523 (1) Å below the planar (O1/O2/C1) carboxylate group. In the TMB anion, the carboxylate group is twisted away from the attached benzene, *A* (C2–C7), ring by 78.80 (14)°, while the benzene and pyridine, *B* (N1/C11–C15), rings are oriented at a dihedral angle of 24.33 (6)°.

3. Supramolecular features

In the crystal structure, $O-H_{\text{coordW}} \cdots O_{\text{noncoordW}}$, $O-H_{\text{noncoordW}} \cdots O_c$, $N-H_{\text{INA}} \cdots O_{\text{noncoordW}}$ and $N-H_{\text{INA}} \cdots O_{\text{INA}}$ (INA = isonicotinamide and noncoordW = non-coordinating water) hydrogen bonds (Table 1) link the molecules (Fig. 2) into

networks parallel to [011], enclosing $R_2^2(6)$, $R_4^1(19)$, $R_4^1(26)$, $R_4^1(28)$, $R_6^0(32)$, $R_8^0(28)$ and $R_8^0(32)$ ring motifs. The crystal structure is further stabilized by a weak $C-H_{\text{INA}} \cdots O_{\text{noncoordW}}$ interaction (Table 1).

4. Hirshfeld surface analysis

A Hirshfeld surface analysis (Hirshfeld, 1977; Spackman & Jayatilaka, 2009) of the title complex was carried out to investigate the locations of the atoms with potential to form hydrogen bonds and the quantitative ratios of these interactions. Conventional mapping of d_{norm} (Fig. 3), together with graphical representation of the Hirshfeld surface (Fig. 4) suggest the locations of the donors and acceptors of intermolecular contacts, which are represented in Fig. 3 as bright-red spots near respective atoms. According to the analysis results, the most important interaction is H···H contributing 59.8% to the overall crystal packing. The next most important interactions are $O \cdots H/H \cdots O$ and $C \cdots H/H \cdots C$ contributing 20.2% and 13.7%, respectively. The weakest intermolecular contacts contributing to the cohesion of the structure are $C \cdots C$, $N \cdots H/H \cdots N$, $C \cdots O/O \cdots C$ and $C \cdots N/N \cdots C$, found to contribute only 3.0, 2.3, 0.6 and 0.4%, respectively. The overall two-dimensional fingerprint plot, Fig. 4*a*, and those delineated into H···H, $O \cdots H/H \cdots O$, $C \cdots H/H \cdots C$, $C \cdots C$, $N \cdots H/H \cdots N$, $C \cdots O/O \cdots C$ and $C \cdots N/N \cdots C$ contacts

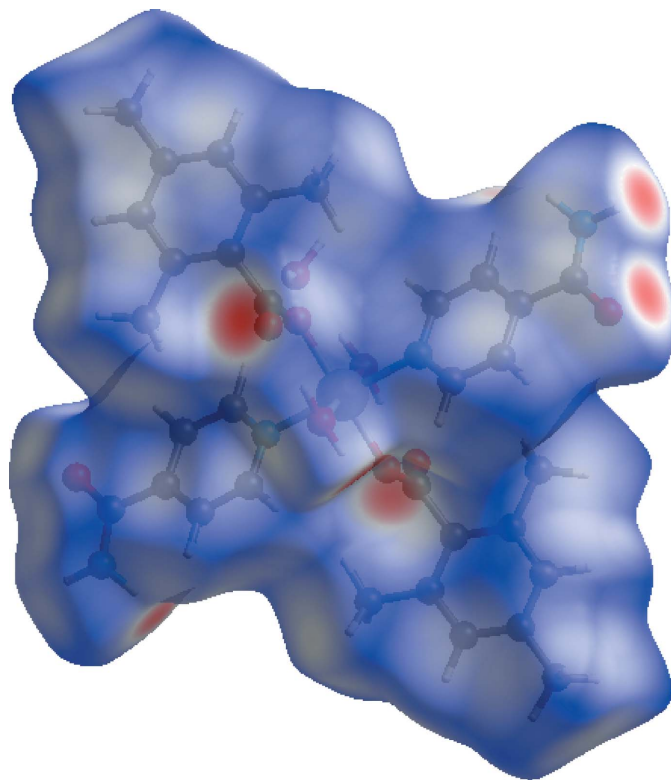


Figure 3
View of the three-dimensional Hirshfeld surface of the title complex plotted over d_{norm} in the range -0.7129 to 1.3644 au.

(McKinnon *et al.*, 2007) are illustrated in Fig. 4 *b–h*, respectively, together with their relative contributions to the Hirshfeld surface, where the significant $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ interactions are indicated by the pair of wings in the two-dimensional fingerprint plot with a prominent long spike at $d_e + d_i \sim 1.0$ Å (Fig. 4c). The presence of these interactions may also be shown by the Hirshfeld surface mapped as a function of curvedness (Fig. 5).

5. Synthesis and crystallization

The title compound was prepared by mixing solutions of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.66 g, 2.5 mmol) in H_2O (50 ml) and isonicotinamide (0.61 g, 5 mmol) in H_2O (25 ml) with sodium 2,4,6-trimethylbenzoate (0.93 g, 5 mmol) in H_2O (150 ml) at room temperature. The mixture was set aside to crystallize at ambient temperature for nine weeks and gave green single crystals (yield: 1.46 g, 83%). Combustion analysis: found; C, 54.70, H, 6.24; N, 8.13%. Calculated: $\text{C}_{32}\text{H}_{42}\text{N}_4\text{NiO}_{10}$ C, 54.80; H, 6.04; N, 7.99%. FT-IR: 3354, 3197, 2235, 1949, 1855, 1698, 1934, 1612, 1557, 1415, 1226, 1182, 1148, 1115, 1096, 1066, 1041, 1017, 985, 885, 855, 792, 772, 747, 682, 660, 638, 615, 520, 443 cm^{-1} .

6. Refinement

The experimental details including the crystal data, data collection and refinement are summarized in Table 2. H atoms

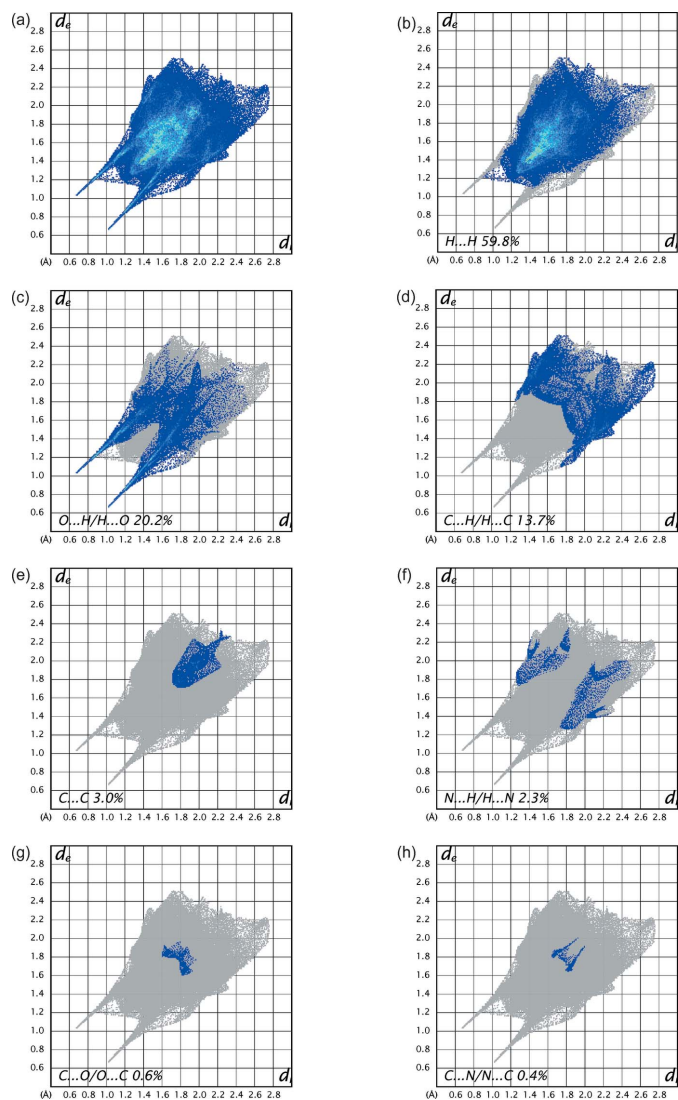


Figure 4
The full two-dimensional fingerprint plots from Hirshfeld analysis of the title complex, showing (a) all interactions, and delineated into (b) $\text{H}\cdots\text{H}$, (c) $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$, (d) $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$, (e) $\text{C}\cdots\text{C}$, (f) $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$, (g) $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$ and (h) $\text{C}\cdots\text{N}/\text{N}\cdots\text{C}$ interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

of NH_2 groups and water molecules were located in difference Fourier maps and refined freely. The C-bound H atoms were positioned geometrically with $\text{C}-\text{H} = 0.93$ and 0.96 Å for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = k \times U_{\text{eq}}(\text{C})$, where $k = 1.5$ for methyl H atoms and $k = 1.2$ for aromatic H atoms. The maximum and minimum residual density peaks were found at 0.83 and 0.78 Å from atoms O1 and O4, respectively.

Acknowledgements

The authors acknowledge the Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the Bruker D8 QUEST diffractometer.

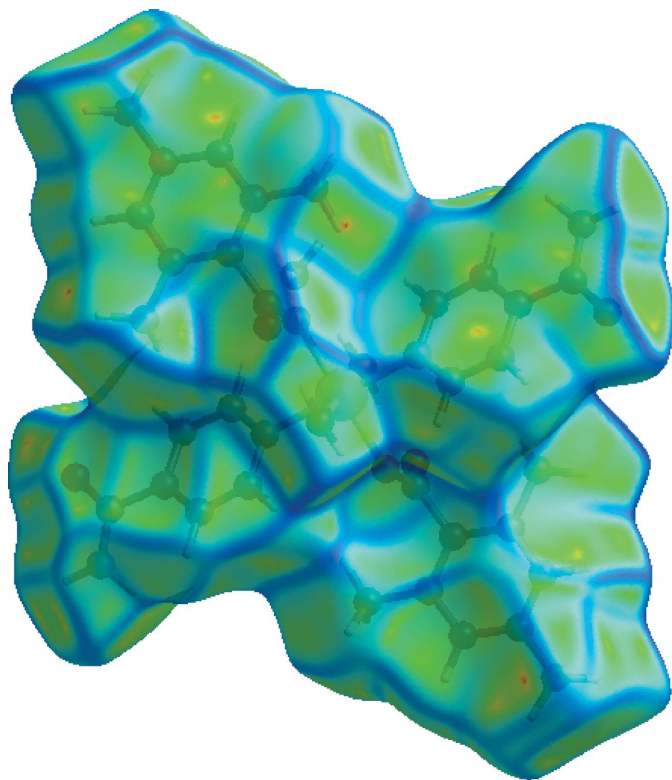


Figure 5
Hirshfeld surface of the title complex plotted over curvedness.

Table 2
Experimental details.

Crystal data	
Chemical formula	[Ni(C ₁₀ H ₁₁ O ₂) ₂ (C ₆ H ₆ N ₂ O) ₂ ·2H ₂ O]
<i>M_r</i>	701.41
Crystal system, space group	Monoclinic, <i>P</i> ₂ / <i>c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.0222 (3), 9.8275 (2), 13.0229 (3)
β (°)	105.645 (3)
<i>V</i> (Å ³)	1728.11 (6)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.62
Crystal size (mm)	0.45 × 0.30 × 0.28
Data collection	
Diffractometer	Bruker SMART BREEZE CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2012)
<i>T_{min}</i> , <i>T_{max}</i>	0.767, 0.845
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	36737, 4290, 3618
<i>R_{int}</i>	0.024
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.667
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.038, 0.103, 1.06
No. of reflections	4290
No. of parameters	241
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.57, -0.42

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

References

- Adiwidjaja, G., Rossmannith, E. & Küppers, H. (1978). *Acta Cryst.* **B34**, 3079–3083.
- Amiraslanov, I. R., Mamedov, Kh. S., Movsumov, E. M., Musaev, F. N. & Nadzhafov, G. N. (1979). *Zh. Strukt. Khim.* **20**, 1075–1080.
- Antolini, L., Battaglia, L. P., Corradi, A. B., Marcotrigiano, G., Menabue, L., Pellacani, G. C. & Saladini, M. (1982). *Inorg. Chem.* **21**, 1391–1395.
- Antsyshkina, A. S., Chiragov, F. M. & Poray-Koshits, M. A. (1980). *Koord. Khim.* **15**, 1098–1103.
- Aşkın, G. Ş., Necefoğlu, H., Tombul, A. M., Dilek, N. & Hökelek, T. (2016). *Acta Cryst.* **E72**, m656–m658.
- Bigoli, F., Braibanti, A., Pellinghelli, M. A. & Tiripicchio, A. (1972). *Acta Cryst.* **B28**, 962–966.
- Bruker (2012). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc. Madison, Wisconsin, USA.
- Capilla, A. V. & Aranda, R. A. (1979). *Cryst. Struct. Commun.* **8**, 795–798.
- Catterick (néé Drew), J., Hursthouse, M. B., New, D. B. & Thornton, P. (1974). *J. Chem. Soc. Chem. Commun.* pp. 843–844.
- Chen, H. J. & Chen, X. M. (2002). *Inorg. Chim. Acta*, **329**, 13–21.
- Clegg, W., Little, I. R. & Straughan, B. P. (1986a). *Acta Cryst.* **C42**, 919–920.
- Clegg, W., Little, I. R. & Straughan, B. P. (1986b). *Acta Cryst.* **C42**, 1701–1703.
- Clegg, W., Little, I. R. & Straughan, B. P. (1987). *Acta Cryst.* **C43**, 456–457.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Guseinov, G. A., Musaev, F. N., Usabaliev, B. T., Amiraslanov, I. R. & Mamedov, Kh. S. (1984). *Koord. Khim.* **10**, 117–122.
- Hauptmann, R., Kondo, M. & Kitagawa, S. (2000). *Z. Kristallogr. New Cryst. Struct.* **215**, 169–172.
- Hirshfeld, H. L. (1977). *Theor. Chim. Acta*, **44**, 129–138.
- Hökelek, T., Dal, H., Tercan, B., Özbek, F. E. & Necefoğlu, H. (2009). *Acta Cryst.* **E65**, m466–m467.
- Hökelek, T., Dal, H., Tercan, B., Tenlik, E. & Necefoğlu, H. (2010). *Acta Cryst.* **E66**, m891–m892.
- Krishnamachari, K. A. V. R. (1974). *Am. J. Clin. Nutr.* **27**, 108–111.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814.
- Nadzhafov, G. N., Shnulin, A. N. & Mamedov, Kh. S. (1981). *Zh. Strukt. Khim.* **22**, 124–128.
- Necefoğlu, H., Çimen, E., Tercan, B., Ermiş, E. & Hökelek, T. (2010). *Acta Cryst.* **E66**, m361–m362.
- Niekerk, J. N. van, Schoening, F. R. L. & Talbot, J. H. (1953). *Acta Cryst.* **6**, 720–723.
- Sertçelik, M., Çaylak, Delibaş, N., Necefoğlu, H. & Hökelek, T. (2012). *Acta Cryst.* **E68**, m946–m947.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shnulin, A. N., Nadzhafov, G. N., Amiraslanov, I. R., Usabaliev, B. T. & Mamedov, Kh. S. (1981). *Koord. Khim.* **7**, 1409–1416.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Tercan, B., Hökelek, T., Aybirdi, Ö. & Necefoğlu, H. (2009). *Acta Cryst.* **E65**, m109–m110.
- Usabaliev, B. T., Guliev, F. I., Musaev, F. N., Ganbarov, D. M., Ashurova, S. A. & Movsumov, E. M. (1992). *Zh. Strukt. Khim.* **33**, m203–m207.
- Wright, W. B. & King, G. S. D. (1954). *Acta Cryst.* **7**, 283–288.
- Xu, T.-G. & Xu, D.-J. (2004). *Acta Cryst.* **E60**, m1462–m1464.
- You, K.-S., Arnold, L. J. Jr, Allison, W. S. & Kaplan, N. O. (1978). *Trends Biochem. Sci.* **3**, 265–268.
- Zhang, X.-Y., Liu, Z.-Y., Liu, Z.-Y., Yang, E.-C. & Zhao, X.-J. (2013). *Z. Anorg. Allg. Chem.* **639**, 974–981.

supporting information

Acta Cryst. (2017). E73, 1237-1241 [https://doi.org/10.1107/S205698901701060X]

Crystal structure and Hirshfeld surface analysis of diaquabis(isonicotinamide- κ N)bis(2,4,6-trimethylbenzoato- κ O¹)nickel(II) dihydrate

Tuncer Hökelek, Gizem Sertkaya, Ezgi Ay, Safiye Özkaya and Hacali Necefoğlu

Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

Diaquabis(isonicotinamide- κ N)bis(2,4,6-trimethylbenzoato- κ O¹)nickel(II) dihydrate

Crystal data

[Ni(C₁₀H₁₁O₂)₂(C₆H₆N₂O)₂(H₂O)₂] \cdot 2H₂O

$M_r = 701.41$

Monoclinic, $P2_1/c$

$a = 14.0222$ (3) Å

$b = 9.8275$ (2) Å

$c = 13.0229$ (3) Å

$\beta = 105.645$ (3)°

$V = 1728.11$ (6) Å³

$Z = 2$

$F(000) = 740$

$D_x = 1.348$ Mg m⁻³

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

Cell parameters from 9322 reflections

$\theta = 2.6$ – 28.3 °

$\mu = 0.62$ mm⁻¹

$T = 296$ K

Block, translucent light blue

$0.45 \times 0.30 \times 0.28$ mm

Data collection

Bruker SMART BREEZE CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2012)

$T_{\min} = 0.767$, $T_{\max} = 0.845$

36737 measured reflections

4290 independent reflections

3618 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 28.3$ °, $\theta_{\min} = 1.5$ °

$h = -18 \rightarrow 18$

$k = -13 \rightarrow 12$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.103$

$S = 1.06$

4290 reflections

241 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 atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 1.1666P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$$

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.

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 $F^2 > 2\text{sigma}(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.0000	0.5000	0.02665 (10)
O1	0.40085 (14)	0.2668 (2)	0.58794 (12)	0.0658 (5)
O2	0.40320 (9)	0.15459 (13)	0.44114 (9)	0.0320 (3)
O3	0.95561 (10)	0.34236 (17)	0.54825 (15)	0.0584 (4)
O4	0.51379 (13)	0.0578 (2)	0.65335 (12)	0.0498 (4)
H41	0.557 (2)	0.035 (3)	0.701 (2)	0.054 (8)*
H42	0.490 (2)	0.133 (3)	0.653 (2)	0.073 (10)*
O5	0.32828 (12)	0.41847 (15)	0.71977 (12)	0.0435 (3)
H51	0.337 (2)	0.371 (3)	0.772 (2)	0.062 (8)*
H52	0.349 (2)	0.371 (3)	0.676 (2)	0.066 (8)*
N1	0.62368 (11)	0.12585 (16)	0.49343 (12)	0.0332 (3)
N2	0.86640 (15)	0.4682 (2)	0.41092 (17)	0.0486 (4)
H21	0.810 (2)	0.497 (2)	0.378 (2)	0.043 (7)*
H22	0.915 (2)	0.520 (3)	0.420 (2)	0.054 (7)*
C1	0.36860 (13)	0.24339 (18)	0.49098 (14)	0.0323 (4)
C2	0.28216 (13)	0.32228 (18)	0.42324 (14)	0.0335 (4)
C3	0.18589 (14)	0.2849 (2)	0.42355 (17)	0.0411 (4)
C4	0.10724 (16)	0.3481 (2)	0.3512 (2)	0.0538 (6)
H4	0.0429	0.3240	0.3504	0.065*
C5	0.12132 (18)	0.4452 (3)	0.2806 (2)	0.0576 (6)
C6	0.2168 (2)	0.4839 (2)	0.28483 (19)	0.0534 (6)
H6	0.2268	0.5519	0.2392	0.064*
C7	0.29841 (15)	0.4242 (2)	0.35545 (16)	0.0422 (4)
C8	0.16723 (18)	0.1801 (3)	0.5003 (2)	0.0594 (6)
H8A	0.2090	0.1984	0.5705	0.089*
H8B	0.1817	0.0912	0.4780	0.089*
H8C	0.0991	0.1841	0.5013	0.089*
C9	0.0339 (3)	0.5094 (4)	0.2002 (3)	0.0906 (12)
H9A	0.0563	0.5862	0.1675	0.136*
H9B	-0.0142	0.5388	0.2358	0.136*
H9C	0.0044	0.4438	0.1464	0.136*
C10	0.4011 (2)	0.4727 (3)	0.3593 (2)	0.0700 (8)

H10A	0.4484	0.4047	0.3928	0.105*
H10B	0.4146	0.5557	0.3996	0.105*
H10C	0.4057	0.4887	0.2881	0.105*
C11	0.62245 (14)	0.2010 (2)	0.40774 (16)	0.0406 (4)
H11	0.5659	0.1991	0.3505	0.049*
C12	0.70084 (14)	0.2816 (2)	0.39966 (17)	0.0430 (4)
H12	0.6966	0.3317	0.3380	0.052*
C13	0.78570 (13)	0.28715 (19)	0.48380 (16)	0.0358 (4)
C14	0.78705 (14)	0.2095 (2)	0.57270 (17)	0.0445 (5)
H14	0.8426	0.2098	0.6310	0.053*
C15	0.70590 (14)	0.1317 (2)	0.57467 (16)	0.0431 (4)
H15	0.7083	0.0807	0.6354	0.052*
C16	0.87691 (14)	0.3701 (2)	0.48379 (18)	0.0418 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.02458 (15)	0.03057 (17)	0.02553 (15)	0.00352 (11)	0.00801 (11)	0.00199 (11)
O1	0.0765 (11)	0.0751 (12)	0.0351 (7)	0.0410 (10)	-0.0032 (7)	-0.0140 (8)
O2	0.0322 (6)	0.0340 (6)	0.0301 (6)	0.0082 (5)	0.0092 (5)	0.0018 (5)
O3	0.0294 (7)	0.0551 (10)	0.0858 (12)	-0.0053 (6)	0.0070 (7)	0.0178 (9)
O4	0.0576 (10)	0.0612 (11)	0.0275 (7)	0.0245 (8)	0.0059 (6)	-0.0006 (7)
O5	0.0552 (9)	0.0393 (8)	0.0330 (7)	0.0042 (6)	0.0067 (6)	-0.0031 (6)
N1	0.0285 (7)	0.0329 (8)	0.0388 (8)	-0.0003 (6)	0.0105 (6)	0.0041 (6)
N2	0.0338 (9)	0.0453 (10)	0.0666 (12)	-0.0084 (8)	0.0135 (8)	0.0108 (9)
C1	0.0318 (8)	0.0314 (8)	0.0334 (8)	0.0046 (7)	0.0085 (7)	-0.0008 (7)
C2	0.0341 (9)	0.0327 (9)	0.0328 (8)	0.0089 (7)	0.0073 (7)	-0.0035 (7)
C3	0.0358 (9)	0.0368 (10)	0.0482 (11)	0.0035 (8)	0.0067 (8)	-0.0054 (8)
C4	0.0344 (10)	0.0508 (13)	0.0680 (14)	0.0070 (9)	-0.0001 (9)	-0.0077 (11)
C5	0.0528 (13)	0.0517 (13)	0.0558 (13)	0.0194 (11)	-0.0068 (10)	-0.0016 (11)
C6	0.0654 (15)	0.0480 (13)	0.0434 (11)	0.0162 (10)	0.0087 (10)	0.0085 (9)
C7	0.0453 (11)	0.0434 (11)	0.0391 (10)	0.0097 (9)	0.0134 (8)	0.0032 (8)
C8	0.0480 (13)	0.0516 (14)	0.0794 (17)	-0.0059 (10)	0.0186 (12)	0.0066 (12)
C9	0.0697 (19)	0.093 (3)	0.085 (2)	0.0307 (17)	-0.0198 (17)	0.0133 (18)
C10	0.0578 (15)	0.0815 (19)	0.0781 (19)	0.0036 (13)	0.0313 (14)	0.0291 (15)
C11	0.0306 (9)	0.0450 (11)	0.0426 (10)	-0.0028 (8)	0.0038 (7)	0.0100 (8)
C12	0.0373 (10)	0.0421 (11)	0.0480 (11)	-0.0047 (8)	0.0090 (8)	0.0142 (9)
C13	0.0288 (8)	0.0304 (9)	0.0497 (10)	-0.0006 (7)	0.0132 (7)	0.0020 (8)
C14	0.0323 (9)	0.0494 (12)	0.0471 (11)	-0.0063 (8)	0.0025 (8)	0.0087 (9)
C15	0.0362 (9)	0.0495 (11)	0.0413 (10)	-0.0058 (8)	0.0063 (8)	0.0110 (9)
C16	0.0308 (9)	0.0366 (10)	0.0602 (12)	-0.0033 (7)	0.0161 (8)	0.0015 (9)

Geometric parameters (Å, °)

Ni1—O2	2.0438 (12)	C4—H4	0.9300
Ni1—O2 ⁱ	2.0438 (12)	C5—C6	1.379 (4)
Ni1—O4	2.0346 (14)	C5—C9	1.518 (3)
Ni1—O4 ⁱ	2.0346 (14)	C6—H6	0.9300

Ni1—N1	2.1506 (15)	C7—C6	1.390 (3)
Ni1—N1 ⁱ	2.1506 (15)	C7—C10	1.504 (3)
O1—C1	1.242 (2)	C8—H8A	0.9600
O2—C1	1.260 (2)	C8—H8B	0.9600
O3—C16	1.224 (2)	C8—H8C	0.9600
O4—H41	0.78 (3)	C9—H9A	0.9600
O4—H42	0.81 (3)	C9—H9B	0.9600
O5—H51	0.81 (3)	C9—H9C	0.9600
O5—H52	0.84 (3)	C10—H10A	0.9600
N1—C11	1.334 (2)	C10—H10B	0.9600
N1—C15	1.339 (2)	C10—H10C	0.9600
N2—C16	1.333 (3)	C11—C12	1.381 (3)
N2—H21	0.84 (3)	C11—H11	0.9300
N2—H22	0.84 (3)	C12—H12	0.9300
C1—C2	1.507 (2)	C13—C12	1.384 (3)
C2—C3	1.400 (3)	C13—C14	1.382 (3)
C2—C7	1.394 (3)	C13—C16	1.517 (2)
C3—C4	1.389 (3)	C14—H14	0.9300
C3—C8	1.506 (3)	C15—C14	1.377 (3)
C4—C5	1.375 (4)	C15—H15	0.9300
O2 ⁱ —Ni1—O2	180.0	C5—C6—H6	119.1
O2—Ni1—N1	91.07 (5)	C7—C6—H6	119.1
O2 ⁱ —Ni1—N1	88.93 (5)	C2—C7—C10	121.65 (19)
O2—Ni1—N1 ⁱ	88.93 (5)	C6—C7—C2	118.4 (2)
O2 ⁱ —Ni1—N1 ⁱ	91.07 (5)	C6—C7—C10	119.9 (2)
O4—Ni1—O2	92.21 (6)	C3—C8—H8A	109.5
O4 ⁱ —Ni1—O2	87.79 (6)	C3—C8—H8B	109.5
O4—Ni1—O2 ⁱ	87.79 (6)	C3—C8—H8C	109.5
O4 ⁱ —Ni1—O2 ⁱ	92.21 (6)	H8A—C8—H8B	109.5
O4—Ni1—O4 ⁱ	180.0	H8A—C8—H8C	109.5
O4—Ni1—N1	90.82 (7)	H8B—C8—H8C	109.5
O4 ⁱ —Ni1—N1	89.18 (7)	C5—C9—H9A	109.5
O4—Ni1—N1 ⁱ	89.18 (7)	C5—C9—H9B	109.5
O4 ⁱ —Ni1—N1 ⁱ	90.82 (7)	C5—C9—H9C	109.5
N1—Ni1—N1 ⁱ	180.0	H9A—C9—H9B	109.5
C1—O2—Ni1	129.09 (11)	H9A—C9—H9C	109.5
Ni1—O4—H41	123 (2)	H9B—C9—H9C	109.5
Ni1—O4—H42	109 (2)	C7—C10—H10A	109.5
H41—O4—H42	120 (3)	C7—C10—H10B	109.5
H52—O5—H51	104 (3)	C7—C10—H10C	109.5
C11—N1—Ni1	121.52 (12)	H10A—C10—H10B	109.5
C11—N1—C15	116.82 (16)	H10A—C10—H10C	109.5
C15—N1—Ni1	121.66 (12)	H10B—C10—H10C	109.5
C16—N2—H21	121.3 (17)	N1—C11—C12	123.34 (18)
C16—N2—H22	114.1 (19)	N1—C11—H11	118.3
H21—N2—H22	119 (2)	C12—C11—H11	118.3
O1—C1—O2	124.52 (17)	C11—C12—C13	119.62 (18)

O1—C1—C2	120.95 (16)	C11—C12—H12	120.2
O2—C1—C2	114.53 (15)	C13—C12—H12	120.2
C3—C2—C1	119.14 (17)	C12—C13—C16	124.47 (18)
C7—C2—C1	119.82 (17)	C14—C13—C12	117.11 (17)
C7—C2—C3	120.86 (17)	C14—C13—C16	118.41 (17)
C2—C3—C8	121.44 (18)	C13—C14—H14	120.1
C4—C3—C2	118.0 (2)	C15—C14—C13	119.83 (18)
C4—C3—C8	120.5 (2)	C15—C14—H14	120.1
C3—C4—H4	118.9	N1—C15—C14	123.28 (18)
C5—C4—C3	122.2 (2)	N1—C15—H15	118.4
C5—C4—H4	118.9	C14—C15—H15	118.4
C4—C5—C6	118.6 (2)	O3—C16—N2	123.77 (19)
C4—C5—C9	121.0 (3)	O3—C16—C13	118.98 (18)
C6—C5—C9	120.5 (3)	N2—C16—C13	117.23 (18)
C5—C6—C7	121.8 (2)		
O4—Ni1—O2—C1	-1.87 (16)	C7—C2—C3—C4	2.7 (3)
O4 ⁱ —Ni1—O2—C1	178.13 (16)	C7—C2—C3—C8	-176.8 (2)
N1—Ni1—O2—C1	-92.74 (15)	C1—C2—C7—C6	172.41 (18)
N1 ⁱ —Ni1—O2—C1	87.26 (15)	C1—C2—C7—C10	-9.2 (3)
O2—Ni1—N1—C11	-45.97 (15)	C3—C2—C7—C6	-2.7 (3)
O2 ⁱ —Ni1—N1—C11	134.03 (15)	C3—C2—C7—C10	175.6 (2)
O2—Ni1—N1—C15	134.61 (16)	C2—C3—C4—C5	-0.2 (3)
O2 ⁱ —Ni1—N1—C15	-45.39 (16)	C8—C3—C4—C5	179.3 (2)
O4—Ni1—N1—C11	-138.19 (16)	C3—C4—C5—C6	-2.3 (4)
O4 ⁱ —Ni1—N1—C11	41.81 (16)	C3—C4—C5—C9	178.1 (3)
O4—Ni1—N1—C15	42.39 (16)	C4—C5—C6—C7	2.3 (4)
O4 ⁱ —Ni1—N1—C15	-137.61 (16)	C9—C5—C6—C7	-178.1 (3)
Ni1—O2—C1—O1	12.8 (3)	C2—C7—C6—C5	0.2 (3)
Ni1—O2—C1—C2	-167.00 (12)	C10—C7—C6—C5	-178.2 (2)
Ni1—N1—C11—C12	-178.99 (16)	N1—C11—C12—C13	-0.4 (3)
C15—N1—C11—C12	0.5 (3)	C14—C13—C12—C11	0.3 (3)
Ni1—N1—C15—C14	179.01 (17)	C16—C13—C12—C11	179.13 (19)
C11—N1—C15—C14	-0.4 (3)	C12—C13—C14—C15	-0.3 (3)
O1—C1—C2—C3	-81.0 (3)	C16—C13—C14—C15	-179.2 (2)
O1—C1—C2—C7	103.8 (2)	C12—C13—C16—O3	-161.4 (2)
O2—C1—C2—C3	98.9 (2)	C12—C13—C16—N2	17.2 (3)
O2—C1—C2—C7	-76.3 (2)	C14—C13—C16—O3	17.4 (3)
C1—C2—C3—C4	-172.43 (18)	C14—C13—C16—N2	-164.0 (2)
C1—C2—C3—C8	8.1 (3)	N1—C15—C14—C13	0.4 (4)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H21 \cdots O5 ⁱⁱ	0.84 (3)	2.18 (3)	3.014 (3)	174 (2)
N2—H22 \cdots O3 ⁱⁱⁱ	0.83 (3)	2.21 (3)	3.043 (3)	177 (2)

O4—H41···O5 ^{iv}	0.77 (3)	2.02 (3)	2.745 (2)	157 (3)
O4—H42···O1	0.81 (3)	1.85 (3)	2.593 (3)	151 (3)
O5—H51···O2 ^v	0.81 (3)	2.16 (3)	2.8804 (19)	148 (3)
O5—H52···O1	0.85 (3)	1.83 (3)	2.673 (2)	176 (2)
C12—H12···O5 ⁱⁱ	0.93	2.56	3.307 (2)	137

Symmetry codes: (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+1, y-1/2, -z+3/2$; (v) $x, -y+1/2, z+1/2$.