Synthesis, crystal structure and Hirshfeld surface analysis of hexaaquanickel(II) bis(4-hydroxybenzoate) dihydrate

Abror Ruzmetov, Aziz Ibragimov, Jamshid Ashurov, Zebo Boltaeva, Bakhtiyar Ibragimov and Sultan Usmanov

*Institute of General and Inorganic Chemistry, Academy of Sciences of Uzbekistan, 100170, M. Ulugbek Str 77a, Tashkent, Uzbekistan, †Institute of Bioorganic Chemistry, Academy of Sciences of Uzbekistan, 100125, Kh. Abdullaev Str 83, Tashkent, Uzbekistan, and ‡Institute of Chemical Sciences of Kazakhstan NAS, Walikhanov str. 106, Almaty, 050010, Kazakhstan. *Correspondence e-mail: atom.uz@mail.ru

The title compound, [Ni(H2O)6](PHB)2.2H2O (I) (PHB = 4-hydroxybenzoate, C7H5O3), was obtained by the reaction of NiCl2, 4-hydroxybenzoic acid (PHBA) and monoethanolamine in aqueous ethanol solution. The NiII ion is coordinated by six water molecules and is located on an inversion center. The outer coordination sphere in the asymmetric unit comprises one PHB anion and one water molecule, i.e. the compound is a salt and a hydrate consisting of three components. In the crystal, the components are packed into an intermolecular network stabilized by O—H⋯O hydrogen bonds. A comprehensive Hirshfeld surface analysis was carried out to investigate the intermolecular interactions in detail.

1. Chemical context

Para-hydroxybenzoic acid (PHBA) is a natural compound found in carrots, oil palm, grapes and others (Manuja et al., 2013). It demonstrates a wide spectrum of biological actions including antimicrobial, antifungal, antialgal, and antiviral activity, the regulation of plant growth and other types of bioactivities (Manuja et al., 2013; Cho et al., 1998; Sytar et al., 2012). As a result of the presence of carboxyl and hydroxyl groups, PHBA can easily form metal complexes (Lo et al., 2020; Sekine et al., 2018; Gomathi & Muthiah, 2013; Ibragimov et al., 2017a,b). The biological properties of ligand compounds, e.g. benzoic acid derivatives, may be enhanced by metal complex formation (Tran et al., 2020; Hassan et al., 2020). The improvement of the biological action may be even more pronounced when an auxiliary ligand with the same bioactivity is inserted into the coordination sphere alongside the target ligand (Ibragimov et al., 2017c). Monoethanolamine (MEA), which is found in a number of food items such as daikon radish, caraway, muscadine grape, etc. has noticeable antimicrobial (Zardini et al., 2014), plant growth (Bergmann & Eckert, 1990) and other types of activities (Moussa et al., 2019). It therefore appeared to be a suitable auxiliary ligand for the bioactivity enhancement of PHBA.

It can be anticipated that mixing a Brønsted base (MEA) with a Brønsted acid (PHBA) in a reaction medium also containing a metal salt (NiCl2) may lead to the formation of different types of compounds: (a) the desired mixed-ligand Ni complex with MEA in neutral and PHBA in carboxylate forms; (b) both ligands coordinated in a neutral form with chlorine ions residing in the outer coordination sphere for
compensation of the positive charge of the central nickel ion; (c) homoleptic complexes or those with only one organic ligand type plus water of coordination (and with or without anions in the outer coordination sphere for potentially needed charge compensation); or (d) a strictly organic salt between monoethanolammonium (i.e. protonated amine) and para-hydroxybenzoate (i.e. deprotonated acid, PHB). However, we have obtained (e), a supramolecular complex (I) based on the Ni\(^{II}\) ion with six coordinated water molecules, two para-hydroxybenzoate anions in the outer coordination sphere and two lattice solvent water molecules.

We presume that this structure is realized due to the energetic favorability of the obtained complex, in particular in the solid state, since the formation of the hexaqua nickel(II) cation opens up the possibility of generating a multitude of stabilizing intermolecular hydrogen bonds. The Brønsted acid–base reaction between the two molecules intended as ligands apparently precedes complexation and/or crystal-ization and monoethanolamine or its protonated cationic cations interact with the anions through the formation of O\(_{7}\)–H\(_{7}\)B hydrogen bonds (Table 1) with an energetic favorability of the obtained complex, in particular in the

| Table 1 Hydrogen-bond geometry (Å, \(^{\circ}\)). |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| D–H⋅⋅⋅A          | D–H             | H⋅⋅⋅A           | D⋅⋅⋅A           | D–H⋅⋅⋅A         |
| O3–H3⋅⋅⋅O4       | 0.86 (3)        | 1.84 (3)       | 2.655 (2)      | 157 (3)        |
| O4–H4A⋅⋅⋅O5\(^{\#}\)| 0.82 (4)        | 1.97 (4)       | 2.785 (2)      | 173 (4)        |
| O4–H4B⋅⋅⋅O2\(^{\#}\)| 0.87 (3)        | 1.88 (3)       | 2.724 (2)      | 163 (3)        |
| O5–H5A⋅⋅⋅O4\(^{\#}\)| 0.87 (3)        | 1.91 (3)       | 2.770 (2)      | 169 (3)        |
| O5–H5B⋅⋅⋅O1      | 0.92 (4)        | 1.73 (4)       | 2.632 (2)      | 168 (3)        |
| O6–H6A⋅⋅⋅O2\(^{\#}\)| 0.81 (3)        | 1.97 (3)       | 2.779 (2)      | 174 (3)        |
| O6–H6B⋅⋅⋅O2\(^{\#}\)| 0.79 (4)        | 2.00 (4)       | 2.748 (2)      | 157 (4)        |
| O7–H7A⋅⋅⋅O3\(^{\#}\)| 0.84 (3)        | 1.88 (3)       | 2.723 (2)      | 176 (3)        |
| O7–H7B⋅⋅⋅O1\(^{\#}\)| 0.93 (4)        | 1.79 (4)       | 2.675 (2)      | 159 (3)        |

Symmetry codes: (i) \(x, -y + 1/2, z + 1/2\); (ii) \(x, y, -z + 1\); (iii) \(-x + 1, -y + 1, -z + 1\); (iv) \(-x + 1, y - 1, z\); (v) \(x + 1, -y + 1/2, z - 1/2\); (vi) \(-x + 1, -y, -z + 1\);

\([\text{Ni(H}_2\text{O)}_6]^{2+}\) is therefore unaccounted for to date. This communication is, hence, devoted to the crystal structure and comprehensive Hirshfeld surface analysis of the obtained supramolecular complex salt_I.

2. Structural commentary

The molecular structure of I is shown in Fig. 1. The asymmetric unit of the structure consists of half of the nickel complex ion (residing on an inversion center), one para-hydroxybenzoate anion (PHB) and one water molecule. The bond lengths between the metal center and the oxygen donor atoms of the water molecules fall into the small range 2.0483 (13)–2.0893 (13) Å, while the bond angles vary between 88.72 (7) and 91.28 (7)°, i.e. the polyhedron around the central ion takes on the form of a nearly ideal octahedron.

Compensation for the positive charge of the Ni\(^{II}\) ion is achieved with the deprotonation of PHBA molecules during the course of the reaction resulting in the respective carboxylate anions, which are incorporated in the outer coordination sphere. The carboxylate group is nearly but not perfectly coplanar with the aromatic ring evidenced by the corresponding dihedral angle of 12.51 (3)°. The complex cations interact with the anions through the formation of O\(_7\)–H\(_7B\)–O\(_1\)\(^{\#}\) [2.675 (2) Å] and O\(_5\)–H\(_5B\)–O\(_1\) [2.632 (2) Å] hydrogen bonds (Table 1) with an \(R_1(6)\) graph-set notation (Etter et al., 1990).

3. Supramolecular features

There are seven crystallographically independent oxygen atoms in the crystal structure, two of which serve only as hydrogen-bond acceptors (O1 and O2), three are both hydrogen-bond donors and acceptors (O3, O4, O5), and two are only hydrogen-bond donors (O6 and O7). All of the oxygen atoms are involved in relatively short intermolecular hydrogen bonds between the [Ni(H\(_2\)O\(_6\)]\(^{2+}\) cations, the PHB anions and the solvent water molecules. The D⋅⋅⋅A distances of these bonds are in the range 2.632 (2)–2.785 (2) Å (Table 1), which is indicative of sufficiently strong intermolecular inter-actions. The aromatic rings of the PHB anions are arranged in two different angles relative to the cell parameters and with an
angle of $57.15^\circ$ between their respective planes (Fig. 2). Adjacent anions with the same ring alignment adopt opposite orientations (alcohol and carboxylate moieties on opposite sites of the molecules alternate when viewed along the crystallographic $a$-axis). The complex cations are bridged by the length of the 4-hydroxybenzoate anions in the $c$-axis direction. The cations are linked in the $ab$ plane by hydrogen bonds to water molecules and the PHB alcohol and carboxylate moieties. In consequence, layers of organic and inorganic sublattices alternate in the $c$-axis direction. Together, these interactions associate the components into a three-dimensional network (Fig. 2).

4. Database survey
A survey of the Cambridge Structural Database [Groom et al., 2016; accessed January 2022 using ConQuest (Bruno et al., 2002)] reveals that there are 352 hits in the database containing the hexaaquanickel(II) complex ion. Nearly half a century ago, coordination complex formation with benzoic acid derivatives including PHBA was widely studied in the Azerbaijan Institute of Applied Physics. Researchers from this institute synthesized and structurally characterized supramolecular complexes analogous to compound I with magnesium(II) (MGHBZA20; Shnulin et al., 1981), cobalt(II) (MGHBZB20; Shnulin et al., 1981) and manganese(II) (COLWUV; Shnulin et al., 1984), which are all isostructural with the title compound. In addition, the structure of the magnesium(II) complex (AYOJP; Baruah, 2016) is isomorphic with that of compound I. The precision of the previous structure determinations of these compounds were not nearly as high as that of the structure reported here ($R$-factors of 0.07 or more compared to 0.03) while the intermolecular interactions have not yet been assessed quantitatively.

5. Hirshfeld surface analysis
Intermolecular interactions can be assessed quantitatively by carrying out a Hirshfeld surface analysis (Spackman et al., 2021). We have calculated Hirshfeld surfaces and fingerprint plots separately for the PHB anion and $[\text{Ni(H}_2\text{O)}_6]^{2+}$ cation of compound I. The red spots on the surfaces show the predominant strong interactions, which correspond to the O6—

![Figure 2](image)

The packing of I viewed along the $b$-axis direction.

![Figure 3](image)

View of the three-dimensional Hirshfeld surfaces for (a) the PHB anion and (b) the $[\text{Ni(H}_2\text{O)}_6]^{2+}$ cation of the title compound I plotted over $d_{norm}$ in the range $-0.4180$ to $1.3344$ a.u.

![Figure 4](image)

Two-dimensional fingerprint plots for (a) the PHB anion and (b) the $[\text{Ni(H}_2\text{O)}_6]^{2+}$ cation.
Table 2
Experimental details.

| Crystal data | Chemical formula | [Ni(H2O)6](C6H12O6)2·2H2O |
|--------------|------------------|----------------------------|
| M0           |                  | 477.06 |
| Crystal system, space group | Orthorhombic, Pbca |
| Temperature (K) | 293 |
| a, b, c (Å) | 11.0812 (2), 7.63258 (17), 23.7986 (5) |
| V (Å³) | 2012.84 (7) |
| Z       | 4 |
| Radiation type | Cu Kα |
| μ (mm⁻¹) | 2.05 |
| Crystal size (mm) | 0.2 × 0.18 × 0.15 |
| Data collection |  |
| Diffractometer | XtaLAB Synergy, single source at home/near, HyPix3000 |
| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2020) |
| Tmin, Tmax | 0.362, 1.000 |
| No. of measured, independent and observed | 9685, 1949, 1656 |
| Rint | 0.033 |
| (sin θ/λ)max (Å⁻¹) | 0.615 |
| Refinement |  |
| R[F² > 2σ(F²)], wR(F²), S | 0.034, 0.101, 1.05 |
| No. of reflections | 1940 |
| No. of parameters | 169 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| Δρmax, Δρmin (e Å⁻³) | 0.25, -0.45 |

Computer programs: CrysAlis PRO (Rigaku OD, 2020), SHELXT2018/2 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), Mercury (Macrae et al., 2020), and OLEX2 (Dolomanov et al., 2009).

6. Synthesis and crystallization

NiCl₂ (0.130 g, 1.0 mmol) was dissolved in a small amount of water. 4-Hydroxybenzoic acid (0.276 g, 2 mmol) was dissolved in a mixed solvent of 2 ml of absolute alcohol and 2 ml of distilled water. After dropwise addition of the PHBA solution and MEA to the nickel salt solution, the color changed gradually to light green. The resultant solution was stirred for 1 h with a magnetic stirrer at 318 K. The solution was allowed to stand at room temperature in a beaker with small holes in the cover for evaporation. About three weeks later, rectangular block-shaped single crystals of [Ni(H2O)6](PHBA)2(H2O)2 appeared. Analysis calculated: NiC12H26O12: C, 34.22%; H, 6.18%. Found: C, 33.63%; H, 6.25%.

7. Refinement

Crystal data, data collection and structure refinement details for the structure of compound 1 are summarized in Table 2. The hydrogen atoms of water molecules and the hydroxyl group of the PHB anion were located in difference-Fourier maps and refined freely. The H atoms of the benzene ring were calculated geometrically with C—H = 0.93 Å and Uiso(H) = 1.2Ueq(C).

Funding information

This work was supported by Uzbekistan Ministry of Innovation Development (project number F3–20200929348) and program BR10965255 within the framework of program-targeted funding of the Republic of Kazakhstan.

References

Baruah, J. B. (2016). Private communication (refcode AYOJOP). CCDC, Cambridge, England. https://doi.org/10.5517/ccdc.csd.ccpky3
Bednarchuk, T. J., Kinzhymbalo, V. & Pietraszko, A. (2016). Acta Cryst. C72, 432–441.
Bergmann, H. & Eckert, H. (1990). Plant Growth Regul. 9, 1–8.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). Acta Cryst. B58, 389–397.
Cho, J.-Y., Moon, J.-H., Seong, K.-Y. & Park, K.-H. (1998). Biosci. Biotechnol. Biochem. 62, 2273–2276.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). Acta Cryst. B46, 256–262.
Gomathi, S. & Muthiah, P. T. (2013). Acta Cryst. C69, 1498–1502.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.
Hassan, F., Fayez, M. & Abdalla, N. (2020). Open J. Inorg. Nonmetallic Materials, 10, 15–29.
Ibragimov, A. B., Ashurov, J. M., Ibragimov, A. B. & Zakirov, B. S. (2017b). Russ. J. Inorg. Chem. 62, 439–445.
Ibragimov, A. B., Ashurov, J. M., Ibragimov, B. T. & Zakirov, B. S. (2017c). J. Mol. Struct. 1128, 307–316.
Ibragimov, A. B., Ashurov, J. M. & Zakirov, B. S. (2017a). J. Struct. Chem. 58, 588–590.
Ibragimov, A. B., Englert, U., Ashurov, J. M. & Wang, A. (2018). J. Struct. Chem. 59, 411–414.
Lo, K. M., Lee, S. M. & Tiekink, E. R. T. (2020). Z. Krist. New Cryst. Struct. 235, 313–315.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platigs, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). J. Appl. Cryst. 53, 226–235.
Manuja, R., Sachdeva, Sh., Jain, A. & Chaudhary, J. (2013). Int. J. Pharm. Sci. Rev. Res, 22, 109–115.
Moussa, H. R., El-Sayed, M. S. & Ghramh, H. A. (2019). Int. J.Veg. Sci. 18, Article No. 185. https://doi.org/10.1186/s12934-019-1233-7
Rigaku OD (2020). CrysAlis PRO. Rigaku Oxford Diffraction, Yarnton, England.
Sekine, Y., Aliyah, K. H., Shimada, T., Zhang, J., Kosaka, W. & Miyasaka, H. (2018). Chem. Lett. 47, 693–696.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Shnulin, A. N., Nadzhafov, G. N., Amiraslanov, I. R., Usubaliev, B. T. & Mamedov, Kh. S. (1981). Russ. J. Coord. Chem. 7, 1409–1417.
Shnulin, A. N., Nadzhafov, G. N. & Mamedov, Kh. S. (1984). J. Struct. Chem. 25, 421–429.
Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). J. Appl. Cryst. 54, 1006–1011.
Sytar, O., Brestic, M., Rai, M. & Shao, H.-B. (2012). J. Med. Plants Res. 6, 2526–2539.
Tran, Q. H. & Doan, T. T. (2020). New J. Chem. 44, 13036–13045.
Zardini, H. Z., Davarpanah, M., Shanbedi, M., Amiri, A., Maghrebi, M. & Ebrahimi, L. (2014). J. Biomed. Mater. Res. 102, 1774–1781.
Synthesis, crystal structure and Hirshfeld surface analysis of hexaaquanickel(II) bis(4-hydroxybenzoate) dihydrate

Abror Ruzmetov, Aziz Ibragimov, Jamshid Ashurov, Zebo Boltaeva, Bakhtiyar Ibragimov and Sultan Usmanov

Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2020); cell refinement: CrysAlis PRO (Rigaku OD, 2020); data reduction: CrysAlis PRO (Rigaku OD, 2020); program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

Hexaaquanickel(II) bis(4-hydroxybenzoate) dihydrate

Crystal data

[Ni(H₂O)₆](C₇H₅O₃)₂·2H₂O

Mr = 477.06
Orthorhombic, Pbca

a = 11.0812 (2) Å
b = 7.63258 (17) Å
c = 23.7986 (5) Å
V = 2012.84 (7) Å³
Z = 4
F(000) = 1000

Data collection

XtaLAB Synergy, single source at home/near, HyPix3000 diffractometer
Detector resolution: 10.0000 pixels mm⁻¹
ω scans
Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2020)

Tmin = 0.362, Tmax = 1.000

9865 measured reflections
1949 independent reflections
1656 reflections with I > 2σ(I)

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.034
wR(F²) = 0.101
S = 1.05
1949 reflections
169 parameters
0 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(Fo)² + (0.0601P)² + 0.4799P]
where P = (Fo² + 2Fc²)/3

(Δρ)max < 0.001
Δρmax = 0.25 e Å⁻³
Δρmin = −0.43 e Å⁻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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| Atom | x     | y     | z     | Uiso/* | Ueq  |
|------|-------|-------|-------|--------|------|
| Ni1  | 0.500000 | 0.500000 | 0.500000 | 0.03036 (17) |
| O5   | 0.32084 (12) | 0.5623 (2) | 0.48130 (6) | 0.0376 (3) |
| O7   | 0.54536 (14) | 0.5367 (2) | 0.41740 (6) | 0.0398 (3) |
| O6   | 0.46162 (15) | 0.2410 (2) | 0.48559 (7) | 0.0419 (3) |
| O2   | 0.04307 (14) | 0.5293 (2) | 0.58057 (6) | 0.0428 (4) |
| O4   | 0.31243 (14) | 0.6490 (2) | 0.90986 (7) | 0.0480 (4) |
| O3   | 0.12531 (15) | 0.5789 (3) | 0.84390 (6) | 0.0582 (5) |
| O1   | 0.23544 (12) | 0.6102 (2) | 0.58333 (6) | 0.0505 (4) |
| C1   | 0.13366 (16) | 0.5753 (3) | 0.66995 (8) | 0.0345 (4) |
| C2   | 0.22791 (16) | 0.6504 (3) | 0.70019 (8) | 0.0374 (4) |
| H2   | 0.293016 | 0.698597 | 0.680979 | 0.045* |
| C4   | 0.13027 (16) | 0.5798 (3) | 0.78679 (8) | 0.0384 (4) |
| C7   | 0.13809 (17) | 0.5705 (3) | 0.60713 (8) | 0.0376 (4) |
| C3   | 0.22651 (17) | 0.6547 (3) | 0.75802 (8) | 0.0393 (4) |
| H3A  | 0.289389 | 0.707250 | 0.777671 | 0.047* |
| H6   | −0.025565 | 0.450481 | 0.679870 | 0.046* |
| C5   | 0.036000 (19) | 0.5025 (3) | 0.75756 (9) | 0.0418 (5) |
| H5   | −0.028059 | 0.451858 | 0.776878 | 0.050* |
| H6A  | 0.456 (3) | 0.183 (4) | 0.5140 (13) | 0.057 (8)* |
| H5A  | 0.286 (3) | 0.486 (4) | 0.4597 (12) | 0.065 (9)* |
| H7A  | 0.494 (3) | 0.496 (3) | 0.3948 (15) | 0.061 (10)* |
| H6B  | 0.499 (3) | 0.183 (5) | 0.4642 (15) | 0.075 (10)* |
| H7B  | 0.619 (4) | 0.487 (4) | 0.4080 (14) | 0.081 (10)* |
| H5B  | 0.282 (3) | 0.586 (4) | 0.5145 (15) | 0.085 (10)* |
| H4A  | 0.318 (3) | 0.739 (5) | 0.9287 (14) | 0.088 (11)* |
| H4B  | 0.385 (3) | 0.609 (4) | 0.9056 (13) | 0.085 (10)* |
| H3   | 0.192 (3) | 0.619 (4) | 0.8573 (14) | 0.083 (10)* |

Atomic displacement parameters (Å²)

| Atom | U₁₁   | U₂₂   | U₃₃   | U₁₂   | U₁₃   | U₂₃   |
|------|-------|-------|-------|-------|-------|-------|
| Ni1  | 0.0238 (3) | 0.0401 (3) | 0.0272 (3) | 0.00122 (16) | 0.00049 (15) | −0.00160 (16) |
| O5   | 0.0259 (6) | 0.0535 (9) | 0.0333 (7) | 0.0017 (6) | 0.0007 (5) | −0.0023 (6) |
| O7   | 0.0314 (7) | 0.0587 (9) | 0.0293 (7) | 0.0001 (7) | 0.0013 (5) | −0.0014 (6) |
| O6   | 0.0479 (8) | 0.0403 (8) | 0.0376 (8) | −0.0021 (7) | 0.0052 (7) | −0.0043 (7) |
| O2   | 0.0392 (8) | 0.0534 (9) | 0.0357 (8) | 0.0008 (6) | −0.0059 (6) | −0.0053 (6) |
| O4   | 0.0352 (8) | 0.0584 (10) | 0.0505 (9) | −0.0020 (7) | −0.0041 (6) | −0.0072 (7) |
| O3   | 0.0390 (8) | 0.1039 (14) | 0.0317 (7) | −0.0147 (9) | −0.0008 (6) | 0.0051 (8) |

Acta Cryst. (2022). E78, 660-664 sup-2
| Atom | U1  | U2  | U3  | U12 | U13 | U23 |
|------|-----|-----|-----|-----|-----|-----|
| O1   | 0.0332 (7) | 0.0840 (11) | 0.0343 (7) | 0.0053 (7) | 0.0055 (5) | −0.0011 (7) |
| C1   | 0.0287 (8) | 0.0402 (10) | 0.0344 (10) | 0.0023 (8) | 0.0004 (7) | −0.0011 (7) |
| C2   | 0.0299 (9) | 0.0441 (11) | 0.0383 (10) | −0.0054 (8) | 0.0022 (7) | 0.0008 (8) |
| C4   | 0.0309 (9) | 0.0508 (11) | 0.0333 (9) | 0.0010 (9) | −0.0001 (7) | 0.0027 (8) |
| C7   | 0.0320 (9) | 0.0441 (11) | 0.0365 (10) | 0.0075 (8) | −0.0003 (7) | −0.0031 (8) |
| C3   | 0.0318 (9) | 0.0477 (11) | 0.0385 (10) | −0.0071 (8) | −0.0024 (7) | −0.0010 (8) |
| C6   | 0.0279 (9) | 0.0486 (12) | 0.0392 (10) | −0.0037 (8) | −0.0030 (8) | −0.0009 (8) |
| C5   | 0.0283 (9) | 0.0571 (13) | 0.0400 (11) | −0.0059 (8) | 0.0020 (8) | 0.0049 (8) |

**Geometric parameters (Å, °)**

| Bonds/Angles | Length/Value |
|--------------|-------------|
| Ni1—O5i      | 2.0893 (13) |
| Ni1—O5       | 2.0893 (13) |
| Ni1—O7       | 2.0482 (13) |
| Ni1—O7i      | 2.0483 (13) |
| Ni1—O6       | 2.0511 (15) |
| Ni1—O6i      | 2.0511 (15) |
| O5—H5A      | 0.87 (3)   |
| O5—H5B      | 0.92 (4)   |
| O7—H7A      | 0.84 (3)   |
| O7—H7B      | 0.92 (4)   |
| O6—H6A      | 0.81 (3)   |
| O6—H6B      | 0.79 (3)   |
| O2—C7       | 1.268 (2)  |
| O4—H4A      | 0.82 (4)   |
| O4—H4B      | 0.86 (4)   |
| O5—Ni1—O5i  | 180.00 (8) |
| O7—Ni1—O5i  | 90.14 (6)  |
| O7—Ni1—O5   | 89.86 (6)  |
| O7i—Ni1—O5  | 90.14 (6)  |
| O7i—Ni1—O5i | 89.86 (6)  |
| O7—Ni1—O7i  | 180.0      |
| O7i—Ni1—O6i | 91.28 (7)  |
| O7i—Ni1—O6  | 88.72 (7)  |
| O7—Ni1—O6   | 91.28 (7)  |
| O7—Ni1—O6i  | 88.72 (7)  |
| O6—Ni1—O5   | 90.77 (6)  |
| O6—Ni1—O5i  | 89.23 (6)  |
| O6i—Ni1—O5  | 90.77 (6)  |
| O6i—Ni1—O5i | 89.23 (6)  |
| O6—Ni1—O6   | 88.72 (7)  |
| O6—Ni1—O6i  | 88.72 (7)  |
| O5—Ni1—O5   | 180.0      |
| C4—O3—H3    | 1.396 (2)  |
| C3—H3A—O5   | 0.9300     |
| C2—H2—O5    | 1.377 (3)  |
| C2—O3—C4    | 1.390 (3)  |
| C4—C3—C2    | 1.387 (3)  |
| C3—C4—O3    | 0.9300     |
| C6—C5—C4    | 1.382 (3)  |
| C5—C4—O3    | 0.9300     |
| C4—C5—C6    | 1.21 (17)  |
| C5—C6—C1    | 1.21 (17)  |
| C6—C5—C4    | 1.19 (17)  |
| C6—C5—C1    | 1.21 (17)  |
| C5—C6—H6    | 1.377 (3)  |
| C6—C5—C4    | 1.19 (17)  |
| C6—C5—C1    | 1.21 (17)  |

*Acta Cryst. (2022). E78, 660-664*
Ni1—O6—H6A  
114 (2)  
C6—C5—C4  
119.50 (18)
Ni1—O6—H6B  
123 (2)  
C6—C5—H5  
120.3
H6A—O6—H6B  
106 (4)

O3—C4—C3—C2  
179.3 (2)  
C7—C1—C2—C3  
−179.30 (18)
O3—C4—C5—C6  
179.88 (19)  
C7—C1—C6—C5  
178.40 (18)
C1—C2—C3—C4  
1.2 (3)  
C3—C4—C5—C6  
−0.4 (3)
C1—C6—C5—C4  
0.6 (3)  
C6—C1—C2—C3  
−1.0 (3)
C2—C1—C7—O2  
−168.06 (18)  
C6—C1—C7—O2  
13.7 (3)
C2—C1—C7—O1  
10.9 (3)  
C6—C1—C7—O1  
−167.37 (19)
C2—C1—C6—C5  
0.1 (3)  
C5—C4—C3—C2  
−0.5 (3)

Symmetry code: (i) −x+1, −y+1, −z+1.

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|------|-------|---------|
| O3—H3···O4 | 0.86 (3) | 1.84 (3) | 2.655 (2) | 157 (3) |
| O4—H4A···O5ii | 0.82 (4) | 1.97 (4) | 2.785 (2) | 173 (4) |
| O4—H4B···O2iii | 0.87 (3) | 1.88 (3) | 2.724 (2) | 163 (3) |
| O5—H5A···O4iv | 0.87 (3) | 1.91 (3) | 2.770 (2) | 169 (3) |
| O5—H5B···O1 | 0.92 (4) | 1.73 (4) | 2.632 (2) | 168 (3) |
| O6—H6A···O2v | 0.81 (3) | 1.97 (3) | 2.779 (2) | 174 (3) |
| O6—H6B···O2vi | 0.79 (4) | 2.00 (4) | 2.748 (2) | 157 (4) |
| O7—H7A···O3iv | 0.84 (3) | 1.88 (3) | 2.723 (2) | 176 (3) |
| O7—H7B···O1i | 0.93 (4) | 1.79 (4) | 2.675 (2) | 159 (3) |

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