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Tetraaqua[3-oxo-1,3-bis(pyridinium-2-yl)propan-1-olato]nickel(II) tribromide dihydrate

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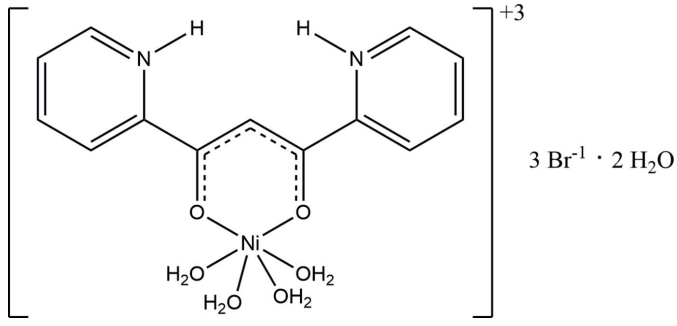
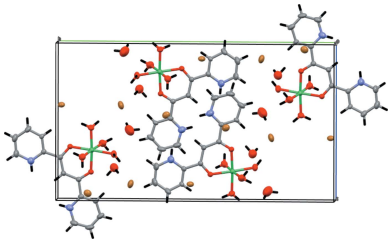
The crystal structure of the title compound, $[Ni(C_{13}H_{11}N_2O_2)(H_2O)_4]Br_3\cdot 2H_2O$, contains an octahedral Ni^{II} atom coordinated to the enol form of 1,3-dipyridylpropane-1,3-dione (dppo) and four water molecules. Both pyridyl rings on the ligand are protonated, forming pyridinium rings and creating an overall ligand charge of +1. The protonated nitrogen-containing rings are involved in hydrogen-bonding interactions with neighoring bromide anions. There are many additional hydrogen-bonding interactions involving coordinated water molecules on the Ni^{II} atom, bromide anions and hydration water molecules.

1. Chemical context

We chose to study 1,3-dipyridylpropane-1,3-dione (dppo) in our ongoing investigations of bridged dipyridyl compounds as ligands for transition metals and rare earths. Previous studies of the di-2-pyridyl ketone (dpk) ligand illustrated that it can undergo a Lewis acid assisted hydration reaction at the ketone to form a diol (Sommerer & Abboud, 1993). This hydration can also occur with Arrhenius acids; however, in the absence of a metal for coordination, the pyridyl N atoms of the resulting diol are protonated (Sommerer *et al.*, 1994). For the dppo in this study, the coordination to the metal center required the presence of an Arrhenius acid (HBr). No hydration of the dione occurred, the ligand adopted the enol form where O atoms behaved as a bidentate ligand, and protonation of the pyridyl rings was observed.





2. Structural commentary

Since the synthesis of the complex was in hydrobromic acid in methanol, the existence of three bromide anions required a trivalent cation. Planar dppo is in its enol form allowing the O atoms to behave as Lewis bases to the nickel center; however, the pyridine rings are both protonated. The H atoms were readily found in difference maps and refined as unconstrained

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.003 (2)	Ni1—O6	2.080 (3)
Ni1—O2	2.006 (2)	Ni1—O5	2.088 (3)
Ni1—O3	2.031 (2)	Ni1—O4	2.088 (2)
O1—Ni1—O2	88.75 (9)	O3—Ni1—O5	93.21 (12)
O1—Ni1—O3	176.19 (9)	O6—Ni1—O5	176.52 (11)
O2—Ni1—O3	87.65 (9)	O1—Ni1—O4	90.82 (9)
O1—Ni1—O6	91.18 (10)	O2—Ni1—O4	177.08 (11)
O2—Ni1—O6	89.88 (10)	O3—Ni1—O4	92.72 (10)
O3—Ni1—O6	87.57 (12)	O6—Ni1—O4	87.24 (11)
O1—Ni1—O5	88.26 (11)	O5—Ni1—O4	89.34 (12)
O2—Ni1—O5	93.54 (11)		

atoms. The organic ligand therefore has an overall +1 charge. There are also four water molecules coordinated to the Ni^{II} atom, thereby completing the octahedral geometry of the $[Ni(C_{13}H_{11}N_2O_2)(H_2O)_4]^{+3}$ cation (Fig. 1). During refinement, two additional waters of hydration were located. There is an angle of 19.48 (7)° between the mean plane of the dipyridinium ligand and the plane defined by the Ni^{II} atom and its four equatorial O atoms. Selected geometric parameters are listed in Table 1.

3. Supramolecular features

A packing diagram of the compound as viewed down (100) is shown in Fig. 2. There are many hydrogen-bonding interactions. The pyridinium H atoms are involved in hydrogen bonding with one of the bromide anions. Bromide anions are also engaged in hydrogen bonding with the waters of hydration and the water molecules coordinated to the Ni^{II} atom. The waters of hydration extend the hydrogen-bonding network by also interacting with the water molecules coordinated to the Ni^{II} center. A summary of the hydrogen-bonding interactions is listed in Table 2.

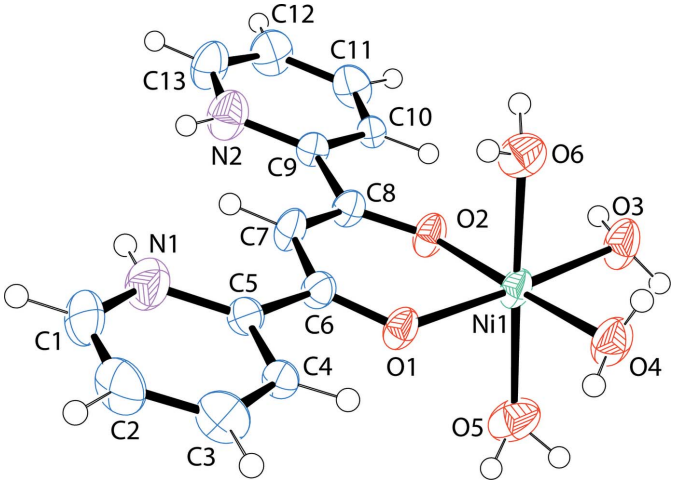


Figure 1
A view of the the title compound, with displacement ellipsoids drawn at the 50% probability level.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br1	0.86	2.94	3.774 (4)	165
N2—H2···Br1	0.86	3.02	3.852 (3)	165
C1—H1*A*···Br2	0.93	2.75	3.567 (3)	147
C4—H4···Br3^{i}	0.93	2.47	3.330 (3)	154
C10—H10···Br2^{ii}	0.93	2.48	3.305 (3)	149
O3—H3*A*···Br2^{ii}	0.84 (2)	2.48 (4)	3.285 (3)	161 (9)
O3—H3*B*···Br3^{iii}	0.83 (2)	2.40 (3)	3.212 (2)	165 (8)
O4—H4*A*···O7^{iv}	0.84 (2)	2.16 (5)	2.917 (4)	150 (9)
O4—H4*B*···Br3^{i}	0.82 (2)	2.48 (3)	3.284 (3)	167 (9)
O5—H5*A*···O7	0.84 (2)	1.99 (3)	2.808 (5)	163 (10)
O5—H5*B*···O8	0.84 (2)	2.29 (6)	3.002 (6)	142 (9)
O6—H6*A*···Br1^{v}	0.84 (2)	2.51 (2)	3.342 (3)	175 (9)
O6—H6*B*···Br2^{v}	0.83 (2)	2.45 (3)	3.266 (3)	165 (9)
O7—H7*A*···Br1^{i}	0.84 (2)	2.59 (6)	3.335 (4)	149 (9)
O7—H7*B*···Br3^{i}	0.85 (2)	2.54 (2)	3.386 (3)	173 (9)
O8—H8*A*···Br3^{vi}	0.85 (2)	3.06 (3)	3.880 (7)	165 (9)
O8—H8*B*···Br1^{iii}	0.84 (2)	2.65 (6)	3.393 (5)	149 (9)

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

4. Database survey

The enol form of dppo has been used to make extended structures with cadmium (Tan *et al.*, 2012), as well as with manganese (Langley *et al.*, 2010). The cadmium structure is a two-dimensional chain of cadmium, chlorides, and ligands. The ligand uses both of its O atoms and pyridyl N atoms to bond to multiple Cd atoms. In Langley, several manganese clusters (with six, seven, and ten manganese atoms) were studied, all having the enol form of the ligand. The ligands vary their coordination, sometimes bonding in a bidentate fashion *via* the two oxygens, sometimes bidentate with a pyridine nitrogen and enol oxygen, and sometimes even monodentate *via* the pyridine nitrogen. Through its multiple modes of bonding in these clusters, the ligand can bond from two to four metal centers.

The ligand has also been shown to use its O atoms and one pyridyl N atom to form a bridging dilanthium complex (Brück *et al.*, 2000) and a bridging triholmium species (Andrews *et al.*,

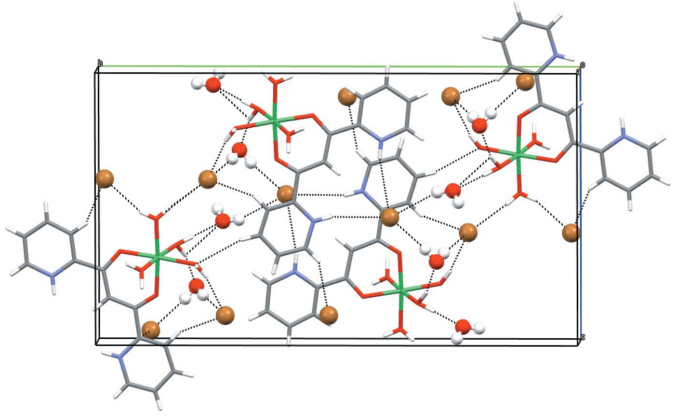


Figure 2
A view of the unit cell along (100). Bromines and free water molecules are shown as balls and sticks and hydrogen bonds as black dashed lines (Macrae *et al.*, 2020).

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Ni(C_{13}H_{11}N_2O_2)(H_2O)_4]$-$Br_3\cdot 2H_2O$
M_r	633.77
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	6.8071 (6), 23.8031 (16), 13.6302 (10)
β (°)	97.476 (9)
V (Å^3)	2189.7 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	6.40
Crystal size (mm)	0.32 × 0.28 × 0.19
Data collection	
Diffractometer	Agilent Xcalibur Sapphire3
Absorption correction	Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min}, T_{max}	0.504, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26929, 7970, 5803
R_{int}	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.781
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.125, 1.05
No. of reflections	7970
No. of parameters	280
No. of restraints	12
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.10, −1.39

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2020) and *OLEX2* (Bourhis *et al.*, 2015).

2009). Finally, the ligand has formed a simpler tris[1,3-bis(-pyridin-2-yl)propane-1,3-dionato]iron(III) compound where the ligand simply bonds to the iron via its O atoms (Lee *et al.*, 2017). Whereas protonation of pyridyl rings on ligands are common in the literature, this structure is the first to display pyridyl protonation for this particular ligand.

5. Synthesis and crystallization

All chemicals were used as received. To 0.1458 g (0.5 mmol) of nickel bromide hydrate (Aldrich) in 35 ml of water was added 0.2424 g (1.0 mmol) of 1,3-di(2-pyridyl)-1,3-propanedione (TCI) under stirring. To this mixture, concentrated HBr (Fisher) was added dropwise until all the ligand had dissolved (pH ∼ 1). This solution was stirred at room temperature for 30 min and filtered to afford an olive-colored solution. Slow evaporation for 28 d yielded pale-red–orange crystals of the title compound. The yield of the product was 64%. The crystals decomposed when a melting-point determination was attempted. FT–IR data for the free ligand and the title compound are included as supporting information and the appearance of a broad band at 3300 cm^{-1} and a broad band with fine structure at 3000 cm^{-1} confirms the presence of water molecules and pyridinium rings.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms on sp^2-hybridized C and N atoms were included in calculated positions, with C—H distances of 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C). Water H atoms were refined applying a distance restraint of 0.84 (2) Å.

Acknowledgements

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supporting information

Acta Cryst. (2020). E**76**, 270-272 [https://doi.org/10.1107/S205698902000081X]

Tetraaqua[3-oxo-1,3-bis(pyridinium-2-yl)propan-1-olato]nickel(II) tribromide dihydrate

Barry L. Westcott, Guy Crundwell and Nilda L. Alicea-Velázquez

Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: OLEX2 (Bourhis *et al.*, 2015).

Tetraaqua[3-oxo-1,3-bis(pyridinium-2-yl)propan-1-olato]nickel(II) tribromide dihydrate

Crystal data

$[Ni(C_{13}H_{11}N_2O_2)(H_2O)_4]3Br{\cdot}2H_2O$
$M_r = 633.77$
Monoclinic, $P2_1/c$
$a = 6.8071$ (6) Å
$b = 23.8031$ (16) Å
$c = 13.6302$ (10) Å
$\beta = 97.476$ (9)°
$V = 2189.7$ (3) Å^3
$Z = 4$
$F(000) = 1248$
$D_x = 1.922$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4741 reflections
$\theta = 4.6$–$32.1°$
$\mu = 6.40$ mm^{-1}
$T = 293$ K
Block, orange
0.32 × 0.28 × 0.19 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 16.1790 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)
$T_{min} = 0.503$, $T_{max} = 1.000$
26929 measured reflections
7970 independent reflections
5803 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 33.7°$, $\theta_{min} = 4.3°$
$h = -10 \rightarrow 10$
$k = -36 \rightarrow 36$
$l = -20 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.125$
$S = 1.05$
7970 reflections
280 parameters
12 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 2.3402P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 1.10$ e Å^{-3}
$\Delta\rho_{min} = -1.39$ 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)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.28363 (5)	0.60904 (2)	0.46388 (3)	0.04291 (10)
Br2	0.22784 (5)	0.48206 (2)	0.10507 (2)	0.03503 (9)
Br3	0.80885 (8)	0.76767 (2)	0.39510 (3)	0.05624 (13)
Ni1	0.15038 (6)	0.37164 (2)	0.81987 (3)	0.02833 (10)
O1	0.2089 (4)	0.37484 (8)	0.67975 (15)	0.0311 (4)
O2	0.2542 (4)	0.45031 (9)	0.83901 (15)	0.0318 (5)
O3	0.0917 (5)	0.37407 (10)	0.96216 (18)	0.0439 (6)
O4	0.0286 (4)	0.29148 (10)	0.79662 (19)	0.0417 (6)
O5	0.4287 (5)	0.33525 (12)	0.8585 (2)	0.0489 (6)
O6	−0.1333 (4)	0.40312 (11)	0.77851 (19)	0.0414 (5)
N1	0.2313 (5)	0.45128 (15)	0.4508 (2)	0.0488 (8)
H1	0.2437	0.4862	0.4669	0.059*
N2	0.3028 (5)	0.59168 (13)	0.7459 (2)	0.0473 (7)
H2	0.3017	0.5882	0.6831	0.057*
C1	0.2240 (6)	0.43458 (18)	0.3530 (2)	0.0464 (9)
H1A	0.2312	0.4615	0.3041	0.056*
C2	0.2062 (7)	0.37877 (18)	0.3273 (2)	0.0480 (9)
H2A	0.2029	0.3677	0.2617	0.058*
C3	0.1935 (6)	0.33996 (17)	0.3999 (2)	0.0432 (8)
H3	0.1814	0.3020	0.3841	0.052*
C4	0.1984 (4)	0.35680 (12)	0.49387 (18)	0.0241 (5)
H4	0.1874	0.3297	0.5420	0.029*
C5	0.2182 (4)	0.41042 (12)	0.52228 (19)	0.0267 (5)
C6	0.2239 (5)	0.41925 (12)	0.6312 (2)	0.0267 (5)
C7	0.2441 (5)	0.47393 (12)	0.6692 (2)	0.0300 (6)
H7	0.2477	0.5037	0.6254	0.036*
C8	0.2593 (4)	0.48545 (11)	0.7704 (2)	0.0264 (5)
C9	0.2832 (4)	0.54534 (11)	0.8042 (2)	0.0246 (5)
C10	0.2865 (4)	0.55252 (11)	0.90202 (18)	0.0216 (5)
H10	0.2701	0.5211	0.9408	0.026*
C11	0.3121 (6)	0.60228 (14)	0.9464 (3)	0.0387 (7)
H11	0.3170	0.6051	1.0148	0.046*
C12	0.3313 (6)	0.64942 (15)	0.8900 (3)	0.0469 (9)
H12	0.3490	0.6845	0.9198	0.056*
C13	0.3243 (6)	0.64421 (14)	0.7904 (3)	0.0450 (8)
H13	0.3339	0.6760	0.7517	0.054*

O7	0.6193 (5)	0.29510 (15)	0.7017 (3)	0.0586 (8)
O8	0.6929 (11)	0.2404 (2)	0.9388 (4)	0.1057 (17)
H3A	0.120 (13)	0.4061 (18)	0.986 (6)	0.159*
H3B	0.140 (12)	0.349 (3)	1.000 (5)	0.159*
H4A	−0.095 (3)	0.289 (4)	0.791 (7)	0.159*
H4B	0.061 (14)	0.272 (3)	0.752 (5)	0.159*
H5A	0.489 (13)	0.317 (4)	0.818 (6)	0.159*
H5B	0.448 (15)	0.304 (2)	0.886 (7)	0.159*
H6A	−0.169 (13)	0.402 (4)	0.7173 (18)	0.159*
H6B	−0.178 (13)	0.432 (2)	0.802 (7)	0.159*
H7A	0.592 (15)	0.319 (3)	0.656 (5)	0.159*
H7B	0.513 (8)	0.281 (4)	0.673 (7)	0.159*
H8A	0.789 (10)	0.252 (4)	0.980 (6)	0.159*
H8B	0.658 (15)	0.2068 (16)	0.945 (8)	0.159*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03826 (18)	0.0478 (2)	0.04137 (18)	−0.00130 (14)	0.00006 (14)	0.00498 (15)
Br2	0.04109 (18)	0.04094 (18)	0.02300 (13)	0.00484 (13)	0.00390 (12)	−0.00060 (11)
Br3	0.0857 (3)	0.02834 (17)	0.0548 (2)	−0.00371 (17)	0.0097 (2)	−0.01026 (15)
Ni1	0.0437 (2)	0.02121 (17)	0.02022 (16)	−0.00070 (14)	0.00474 (15)	0.00139 (12)
O1	0.0497 (13)	0.0228 (9)	0.0210 (9)	0.0008 (9)	0.0051 (9)	0.0011 (7)
O2	0.0510 (13)	0.0230 (9)	0.0213 (9)	−0.0049 (9)	0.0038 (9)	0.0000 (7)
O3	0.0761 (19)	0.0318 (12)	0.0258 (10)	−0.0031 (12)	0.0139 (12)	0.0026 (9)
O4	0.0597 (16)	0.0247 (10)	0.0418 (13)	−0.0045 (11)	0.0105 (12)	−0.0001 (9)
O5	0.0583 (17)	0.0447 (15)	0.0407 (13)	0.0133 (13)	−0.0053 (12)	0.0019 (11)
O6	0.0482 (14)	0.0358 (12)	0.0392 (12)	0.0026 (11)	0.0021 (11)	−0.0038 (10)
N1	0.064 (2)	0.0480 (18)	0.0351 (15)	0.0050 (16)	0.0085 (15)	0.0064 (13)
N2	0.064 (2)	0.0373 (15)	0.0405 (15)	−0.0065 (15)	0.0061 (15)	−0.0003 (13)
C1	0.061 (2)	0.055 (2)	0.0230 (13)	0.0033 (18)	0.0076 (15)	0.0093 (14)
C2	0.058 (2)	0.066 (3)	0.0200 (13)	0.0027 (19)	0.0057 (15)	−0.0077 (14)
C3	0.054 (2)	0.0456 (19)	0.0301 (15)	−0.0022 (16)	0.0045 (15)	−0.0164 (14)
C4	0.0314 (13)	0.0240 (11)	0.0170 (10)	−0.0010 (10)	0.0033 (10)	−0.0048 (9)
C5	0.0314 (14)	0.0292 (13)	0.0193 (10)	0.0021 (11)	0.0029 (10)	−0.0013 (10)
C6	0.0349 (14)	0.0250 (12)	0.0201 (10)	0.0019 (11)	0.0038 (10)	0.0000 (9)
C7	0.0476 (17)	0.0219 (12)	0.0204 (11)	−0.0025 (11)	0.0040 (12)	0.0018 (9)
C8	0.0341 (14)	0.0219 (11)	0.0227 (11)	−0.0020 (10)	0.0021 (11)	−0.0011 (9)
C9	0.0275 (12)	0.0226 (12)	0.0232 (11)	−0.0021 (10)	0.0022 (10)	−0.0023 (9)
C10	0.0260 (12)	0.0190 (11)	0.0202 (10)	−0.0032 (9)	0.0052 (9)	−0.0035 (8)
C11	0.0496 (19)	0.0339 (16)	0.0346 (15)	−0.0085 (14)	0.0135 (15)	−0.0141 (13)
C12	0.062 (2)	0.0276 (16)	0.053 (2)	−0.0092 (15)	0.0142 (18)	−0.0108 (14)
C13	0.065 (2)	0.0242 (14)	0.0465 (19)	−0.0097 (15)	0.0092 (18)	0.0011 (14)
O7	0.0591 (18)	0.0536 (18)	0.0612 (19)	0.0006 (14)	0.0002 (15)	0.0041 (14)
O8	0.161 (5)	0.071 (3)	0.086 (3)	0.024 (3)	0.020 (3)	0.020 (3)

Geometric parameters (Å, º)

Ni1—O1	2.003 (2)	C2—C3	1.365 (6)
Ni1—O2	2.006 (2)	C2—H2A	0.9300
Ni1—O3	2.031 (2)	C3—C4	1.339 (4)
Ni1—O6	2.080 (3)	C3—H3	0.9300
Ni1—O5	2.088 (3)	C4—C5	1.336 (4)
Ni1—O4	2.088 (2)	C4—H4	0.9300
O1—C6	1.258 (3)	C5—C6	1.495 (4)
O2—C8	1.259 (3)	C6—C7	1.401 (4)
O3—H3A	0.84 (2)	C7—C8	1.396 (4)
O3—H3B	0.83 (2)	C7—H7	0.9300
O4—H4A	0.84 (2)	C8—C9	1.501 (4)
O4—H4B	0.82 (2)	C9—C10	1.341 (3)
O5—H5A	0.84 (2)	C10—C11	1.331 (4)
O5—H5B	0.84 (2)	C10—H10	0.9300
O6—H6A	0.84 (2)	C11—C12	1.376 (5)
O6—H6B	0.83 (2)	C11—H11	0.9300
N1—C1	1.386 (5)	C12—C13	1.358 (5)
N1—C5	1.387 (4)	C12—H12	0.9300
N1—H1	0.8600	C13—H13	0.9300
N2—C9	1.376 (4)	O7—H7A	0.84 (2)
N2—C13	1.389 (5)	O7—H7B	0.85 (2)
N2—H2	0.8600	O8—H8A	0.85 (2)
C1—C2	1.375 (6)	O8—H8B	0.84 (2)
C1—H1A	0.9300		
O1—Ni1—O2	88.75 (9)	C3—C2—C1	118.7 (3)
O1—Ni1—O3	176.19 (9)	C3—C2—H2A	120.6
O2—Ni1—O3	87.65 (9)	C1—C2—H2A	120.6
O1—Ni1—O6	91.18 (10)	C4—C3—C2	119.7 (3)
O2—Ni1—O6	89.88 (10)	C4—C3—H3	120.2
O3—Ni1—O6	87.57 (12)	C2—C3—H3	120.2
O1—Ni1—O5	88.26 (11)	C5—C4—C3	123.5 (3)
O2—Ni1—O5	93.54 (11)	C5—C4—H4	118.2
O3—Ni1—O5	93.21 (12)	C3—C4—H4	118.2
O6—Ni1—O5	176.52 (11)	C4—C5—N1	118.7 (3)
O1—Ni1—O4	90.82 (9)	C4—C5—C6	114.3 (2)
O2—Ni1—O4	177.08 (11)	N1—C5—C6	127.1 (3)
O3—Ni1—O4	92.72 (10)	O1—C6—C7	126.6 (3)
O6—Ni1—O4	87.24 (11)	O1—C6—C5	114.3 (2)
O5—Ni1—O4	89.34 (12)	C7—C6—C5	119.1 (2)
C6—O1—Ni1	124.99 (19)	C8—C7—C6	122.6 (3)
C8—O2—Ni1	124.54 (18)	C8—C7—H7	118.7
Ni1—O3—H3A	109 (6)	C6—C7—H7	118.7
Ni1—O3—H3B	117 (6)	O2—C8—C7	126.7 (3)
H3A—O3—H3B	112 (9)	O2—C8—C9	114.5 (2)
Ni1—O4—H4A	118 (7)	C7—C8—C9	118.8 (2)

Ni1—O4—H4B	120 (7)	C10—C9—N2	118.8 (3)
H4A—O4—H4B	104 (8)	C10—C9—C8	114.5 (2)
Ni1—O5—H5A	123 (7)	N2—C9—C8	126.8 (3)
Ni1—O5—H5B	124 (7)	C11—C10—C9	123.3 (3)
H5A—O5—H5B	77 (8)	C11—C10—H10	118.3
Ni1—O6—H6A	114 (6)	C9—C10—H10	118.3
Ni1—O6—H6B	125 (7)	C10—C11—C12	119.2 (3)
H6A—O6—H6B	109 (8)	C10—C11—H11	120.4
C1—N1—C5	118.5 (3)	C12—C11—H11	120.4
C1—N1—H1	120.8	C13—C12—C11	119.4 (3)
C5—N1—H1	120.8	C13—C12—H12	120.3
C9—N2—C13	118.8 (3)	C11—C12—H12	120.3
C9—N2—H2	120.6	C12—C13—N2	120.4 (3)
C13—N2—H2	120.6	C12—C13—H13	119.8
C2—C1—N1	120.9 (3)	N2—C13—H13	119.8
C2—C1—H1A	119.5	H7A—O7—H7B	80 (8)
N1—C1—H1A	119.5	H8A—O8—H8B	116 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br1	0.86	2.94	3.774 (4)	165
N2—H2···Br1	0.86	3.02	3.852 (3)	165
C1—H1*A*···Br2	0.93	2.75	3.567 (3)	147
C4—H4···Br3^{i}	0.93	2.47	3.330 (3)	154
C10—H10···Br2^{ii}	0.93	2.48	3.305 (3)	149
O3—H3*A*···Br2^{ii}	0.84 (2)	2.48 (4)	3.285 (3)	161 (9)
O3—H3*B*···Br3^{iii}	0.83 (2)	2.40 (3)	3.212 (2)	165 (8)
O4—H4*A*···O7^{iv}	0.84 (2)	2.16 (5)	2.917 (4)	150 (9)
O4—H4*B*···Br3^{i}	0.82 (2)	2.48 (3)	3.284 (3)	167 (9)
O5—H5*A*···O7	0.84 (2)	1.99 (3)	2.808 (5)	163 (10)
O5—H5*B*···O8	0.84 (2)	2.29 (6)	3.002 (6)	142 (9)
O6—H6*A*···Br1^{v}	0.84 (2)	2.51 (2)	3.342 (3)	175 (9)
O6—H6*B*···Br2^{v}	0.83 (2)	2.45 (3)	3.266 (3)	165 (9)
O7—H7*A*···Br1^{i}	0.84 (2)	2.59 (6)	3.335 (4)	149 (9)
O7—H7*B*···Br3^{i}	0.85 (2)	2.54 (2)	3.386 (3)	173 (9)
O8—H8*A*···Br3^{vi}	0.85 (2)	3.06 (3)	3.880 (7)	165 (9)
O8—H8*B*···Br1^{iii}	0.84 (2)	2.65 (6)	3.393 (5)	149 (9)

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