

Crystal structure of $[\text{Ni}(\text{OH}_2)_6]\text{Cl}_2 \cdot (18\text{-crown-6})_2 \cdot 2\text{H}_2\text{O}$

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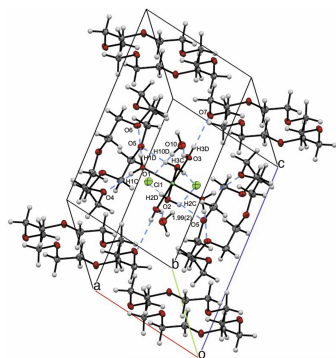
The crystal structure of the title compound, hexaaquanickel(II) dichloride–1,4,7,10,13,16-hexaoxacyclooctadecane–water (1/2/2), $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot 2\text{C}_{12}\text{H}_{24}\text{O}_6 \cdot 2\text{H}_2\text{O}$, is reported. The asymmetric unit contains half of the $\text{Ni}(\text{OH}_2)_6$ moiety with a formula of $\text{C}_{12}\text{H}_{32}\text{ClNi}_{0.50}\text{O}_{10}$ at 105 K and triclinic ($P1$) symmetry. The $[\text{Ni}(\text{OH}_2)_6]^{2+}$ cation has close to ideal octahedral geometry with $\text{O}—\text{Ni}—\text{O}$ bond angles that are within 3° of idealized values. The supramolecular structure includes hydrogen bonding between the water ligands, 18-crown-6 molecules, Cl^- anions, and co-crystallized water solvent. Two crown ether molecules flank the $[\text{Ni}(\text{OH}_2)_6]^{2+}$ molecule at the axial positions in a sandwich-like structure. The relatively symmetric hydrogen-bonding network is enabled by small Cl^- counter-ions and likely influences the more idealized octahedral geometry of $[\text{Ni}(\text{OH}_2)_6]^{2+}$.

1. Chemical context

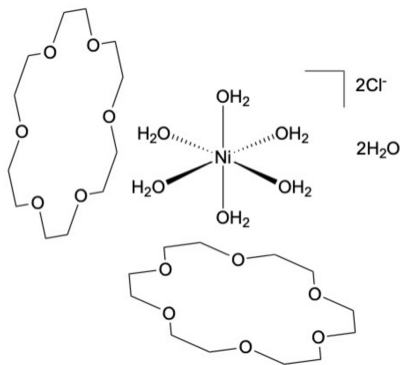
Crown ethers are common chelating agents that are widely used in organometallic chemistry to encapsulate counter-ions for more facile crystallization (Kundu *et al.*, 2019; Tondreau *et al.*, 2013), but crown ethers also have broader applications in materials, sensing, and medicines (Gokel *et al.*, 2004; Li *et al.*, 2017). Among the first reports of using a crown ether as a chelating agent for a metal was in 1967, demonstrating that crown ethers can chelate directly to metals *via* the oxygen atoms, as evidenced by shifts in the IR spectra (Pedersen, 1967). The oxygen atoms on crown ethers can also act as hydrogen-bond acceptors, with some examples of donors being NH_4^+ (Akutagawa *et al.*, 2002), RNH_3^+ (Pedersen, 1967; Shinkai *et al.*, 1985; Sutherland, 1986; Stoddart, 1988; Izatt *et al.*, 1995), R_2NH_2^+ (Kolchinski *et al.*, 1995; Ashton *et al.*, 1997), and $\text{M}—\text{OH}_2$ (Cusack *et al.*, 1984).

18-Crown-6 has also been shown to stabilize octahedral metal complexes *via* hydrogen-bonding networks, for example, in metal nitrate complexes (Junk *et al.*, 1998). The $[\text{18-crown-6}][\text{Ni}(\text{NO}_3)(\text{H}_2\text{O})_5]\text{NO}_3 \cdot \text{H}_2\text{O}$ complex is reported to have a pseudo-octahedral Ni^{II} center, with one nitrate and five water ligands, although the nickel complex was not explicitly discussed in the paper, and the full structural data are not in the Cambridge Structural Database (Junk *et al.*, 1998). The hydrogen-bonding network is reported to be between water ligands and two neighboring 18-crown-6 molecules, the nitrate counter-ion, and water, at distances ranging from 2.679 (9) to 3.05 (1) Å. Water ligands on Ni^{II} have also been shown to act as hydrogen-bond donors intramolecularly (Brazzolotto *et al.*, 2019).

There are few crystallographically characterized systems containing $[\text{Ni}(\text{OH}_2)_6]^{2+}$ and 18-crown-6, with two examples reported in the same study: $[\text{Ni}(\text{OH}_2)_6][\text{ClO}_4]_2 \cdot (18\text{-crown-6})_2 \cdot$



2H₂O and [Ni(OH₂)₆]₃[NiBr₂(H₂O)₄][Br]₆·(18-crown-6)₄·2H₂O (Steed *et al.*, 1998). This current work highlights the effect that a smaller Cl[−] ancillary counter-ion has on the supramolecular structure and octahedral distortion of [Ni(OH₂)₆]²⁺ co-crystallized with 18-crown-6.



2. Structural commentary

Two asymmetric units make up the structure of [Ni(OH₂)₆]₂·Cl₂·(18-crown-6)₂·2H₂O, which has two Cl[−] counter-ions to balance the Ni^{II} center in [Ni(OH₂)₆]²⁺ (Fig. 1). The [Ni(OH₂)₆]²⁺ has close to perfect octahedral geometry with O—Ni—O bond angles of 91.62 (3)° for O1—Ni1—O2, 91.05 (3)° for O1—Ni1—O3, and 92.90 (3)° for O2—Ni1—O2. The bond angles for all *trans*-water substituents on nickel are 180° (O—Ni—O), as a result of the triclinic (*P* $\bar{1}$) symmetry. This represents a much more symmetric [Ni(OH₂)₆]²⁺ cation than the previously reported structure with 18-crown-6, which had *trans* water-ligand angles in the range of 174.43 (7)–178.42 (7)° (Steed *et al.*, 1998).

The Ni—O bond distances are 2.0310 (8) Å for Ni1—O1, 2.0567 (8) Å for Ni1—O2, and 2.0474 (8) Å for Ni1—O3. These distances are consistent with a slight axial compression for Ni1—O1, but it is not as pronounced as the axial Ni—O distance of 2.0066 (16) Å reported for [Ni(OH₂)₆][ClO₄]₂·(18-crown-6)₂·2H₂O (Steed *et al.*, 1998).

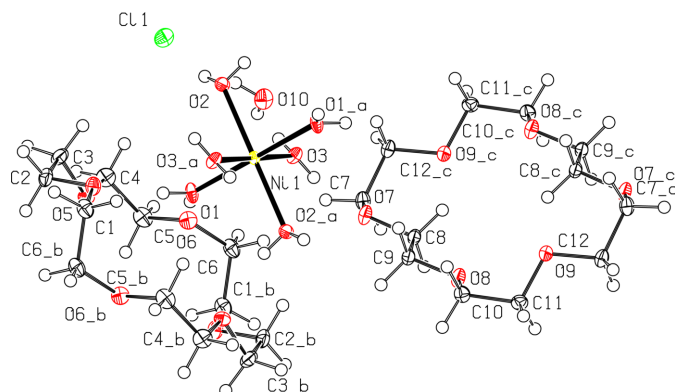


Figure 1
View of [Ni(OH₂)₆]₂·Cl₂·(18-crown-6)₂·2H₂O with 50% probability ellipsoids. H atoms are omitted for clarity.

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1C···O4	0.797 (18)	1.973 (18)	2.7679 (12)	174.7 (17)
O1—H1D···O6	0.780 (18)	1.956 (18)	2.7360 (12)	177.3 (17)
O2—H2C···O5 ⁱ	0.79 (2)	1.99 (2)	2.7695 (12)	167 (1)
O2—H2D···Cl1	0.803 (19)	2.335 (19)	3.1258 (9)	168.6 (16)
O3—H3C···O10	0.82 (2)	1.84 (2)	2.6229 (12)	160 (2)
O3—H3D···O7	0.780 (18)	2.146 (18)	2.8819 (11)	157.4 (17)
O10—H10C···Cl1 ⁱⁱ	0.83 (2)	2.38 (2)	3.2038 (10)	171 (2)
O10—H10D···Cl1	0.86 (2)	2.30 (2)	3.1559 (10)	173 (2)

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

3. Supramolecular features

The supramolecular structure of [Ni(OH₂)₆]₂·Cl₂·(18-crown-6)₂·2H₂O is stabilized *via* extensive hydrogen bonding (Figs. 2 and 3). The differences in Ni—O bond distances are rationalized by differing hydrogen-bonding interactions to each water moiety bound to Ni in the asymmetric unit. The axial water moiety has hydrogen bonding to only 18-crown-6, whereas the equatorial water moieties have hydrogen bonding to 18-crown-6 and chloride or water. The axial water moiety containing O1, H1C, and H1D, has hydrogen bonding to the neighboring 18-crown-6 molecule with distances of 1.973 (18) Å for O4···H1C and 1.956 (18) Å for O6···H1D (Table 1). By contrast, the equatorial water moiety containing O2, H2C, and H2D, has hydrogen bonding to the neighboring 18-crown-6 molecule with a distance of 1.991 (15) Å for O5···H2C, and to one Cl[−] atom with a distance of

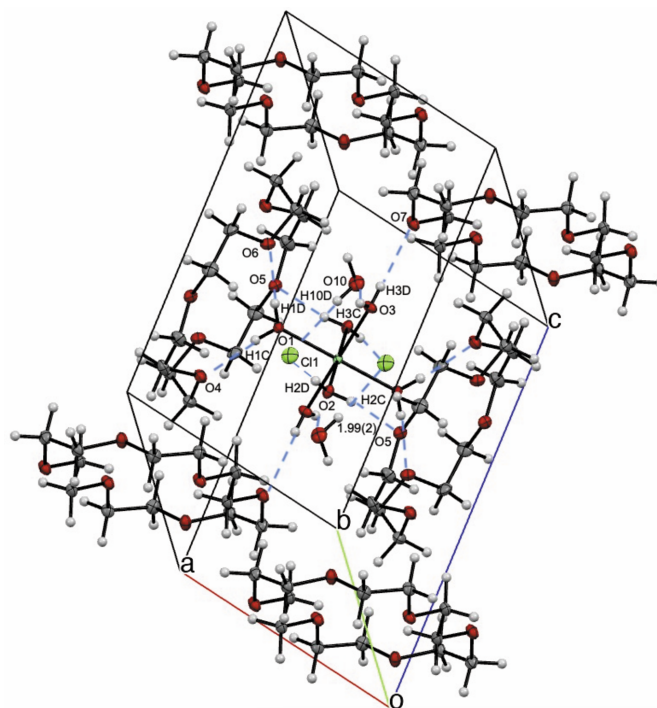


Figure 2
View of the unit cell for [Ni(OH₂)₆]₂·Cl₂·(18-crown-6)₂·2H₂O with 50% probability ellipsoids, highlighting intermolecular distances. Distances including H atoms are listed without standard deviations because the H atoms were positionally fixed. Additional distances are labeled in Fig. 3 for clarity.

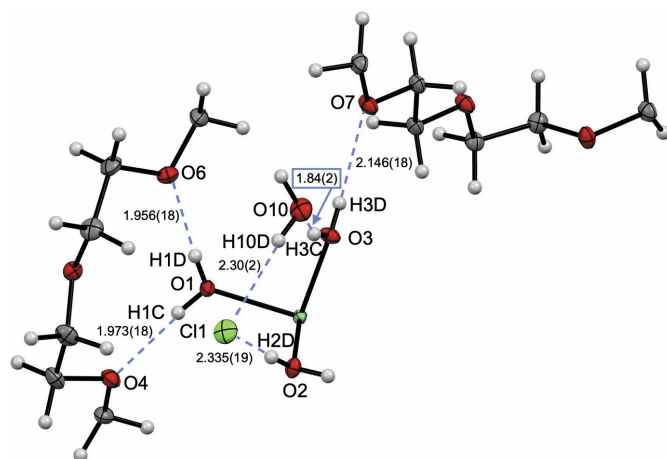


Figure 3

View of the asymmetric unit for $[\text{Ni}(\text{OH}_2)_6]\text{Cl}_2 \cdot (18\text{-crown-6})_2 \cdot 2\text{H}_2\text{O}$ with 50% probability ellipsoids, highlighting intermolecular distances. Distances including H atoms are listed without standard deviations because the H atoms were positionally fixed.

2.335 (19) Å for $\text{Cl1} \cdots \text{H2D}$. The second equatorial water moiety containing O3, H3C, and H3D, has hydrogen bonding to the neighboring 18-crown-6 molecule with a distance of 2.146 (18) Å for $\text{O7} \cdots \text{H3D}$, and to one water molecule with a distance of 1.84 (2) Å for $\text{O10} \cdots \text{H3C}$. Combined, these differing hydrogen-bonding partners for the H_2O ligands result in the varying Ni—O bond distances in $[\text{Ni}(\text{OH}_2)_6]^{2+}$. An additional hydrogen bond stabilizes the structure between H_2O and Cl^- with 2.30 (2) Å for $\text{H10D} \cdots \text{Cl1}$.

The significant effect of the counter-ion on the supramolecular structure and hydrogen bonding is evident from the smaller Cl^- counter-ions as compared to the ClO_4^- counter-

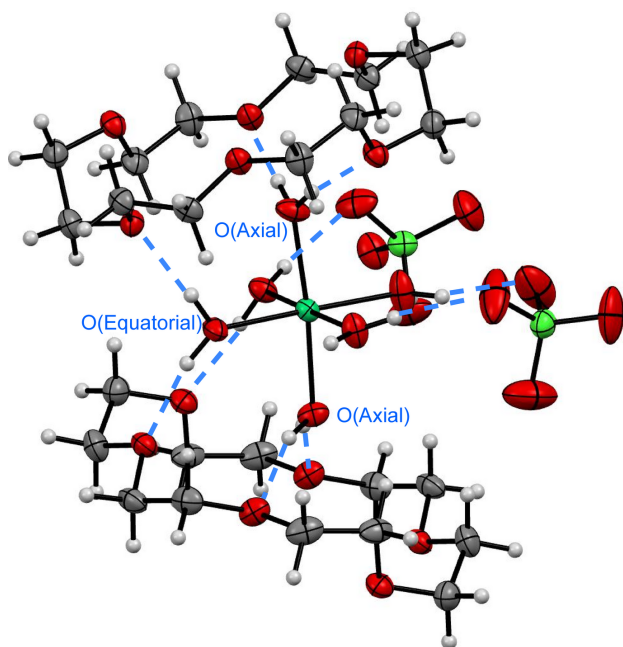


Figure 4

View of $[\text{Ni}(\text{OH}_2)_6][\text{ClO}_4]_2 \cdot (18\text{-crown-6})_2$ (Steed *et al.*, 1998), highlighting hydrogen bonding from axial and equatorial water ligands.

ions in the previously reported structure (Steed *et al.*, 1998). The counter-ion size and hydrogen bonding likely influences the $[\text{Ni}(\text{OH}_2)_6]^{2+}$ geometry and level of distortion from octahedral symmetry. In both structures, each of the axial OH_2 moieties forms two hydrogen bonds the neighboring 18-crown-6 molecule (Figs. 3 and 4). When Cl^- counter-ions are present, one equatorial water forms a hydrogen bond to the top 18-crown-6 molecule, and one equatorial water forms a hydrogen bond to the bottom 18-crown-6 molecule, with both having an additional hydrogen bond each to Cl^- counter-ions. The other two *trans* equatorial water ligands have hydrogen bonds to additional neighboring 18-crown-6 molecules and a water molecule each. The ^1H NMR spectrum in CDCl_3 suggests that at least some of the supramolecular structure is maintained in solution, with two proton signals at 3.52 and 3.58 ppm, assigned to the equatorial water ligands due to lack of HSQC or HMBC carbon correlations. This is significantly shifted from the expected shift for free water in CDCl_3 at 1.56 ppm (Babji *et al.*, 2016), and is consistent with a previous NMR and crystallographic study of $\{[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}\}_n$, where water ligand hydrogen bonding to 18-crown-6 was maintained in non-coordinating solvents (Amini *et al.*, 2006). The overall structure is therefore relatively symmetric with minimal distortion to the octahedral symmetry of $[\text{Ni}(\text{OH}_2)_6]^{2+}$, and NMR data suggest that hydrogen bonding to the 18-crown-6 molecule is preserved in deuterated chloroform solvent.

The structure for $[\text{Ni}(\text{OH}_2)_6][\text{ClO}_4]_2 \cdot (18\text{-crown-6})_2 \cdot 2\text{H}_2\text{O}$ is much less symmetric at a supramolecular level (Fig. 4), which is attributed to the ClO_4^- counter-ions (Steed *et al.*, 1998). One equatorial water ligand forms a hydrogen bond to each of the top and bottom 18-crown-6 molecules, resulting in those molecules being brought closer to each other on one side. The flanking *trans* equatorial water ligands each form a hydrogen bond to a neighboring 18-crown-6 molecule, and a second hydrogen bond to a ClO_4^- counter-ion. This less symmetric network of hydrogen bonding results in stronger distortions in both the Ni—O bond lengths and O—Ni—O bond angles, as compared to the structure with Cl^- counter-ions.

4. Database survey

The Cambridge Structural Database (Groom *et al.*, 2016) has almost 400 structures containing a $\text{Ni}(\text{OH}_2)_6$ moiety; however, only two reported structures were found that contain 18-crown-6 (Web accessed June 3, 2024). The two reported structures are $[\text{Ni}(\text{OH}_2)_6][\text{ClO}_4]_2 \cdot (18\text{-crown-6})_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}(\text{OH}_2)_6]_3[\text{NiBr}_2(\text{H}_2\text{O})_4][\text{Br}]_6 \cdot (18\text{-crown-6})_4 \cdot 2\text{H}_2\text{O}$ (CSD Nos. 113101 and 113105; Steed *et al.*, 1998). By contrast, there are 64 reported structures in the Cambridge Structural Database that contain a $\text{Ni}(\text{OH}_2)_6$ moiety with 15-crown-5 (Web accessed June 3, 2024).

5. Synthesis and crystallization

General considerations. All reagents were purchased from commercial suppliers and used without further purification.

^1H and ^{13}C NMR data were collected on a Varian 400 MHz instrument and referenced to residual CHCl_3 (7.26 ppm). Full NMR data can be accessed through Zenodo (Brannon & Stieber, 2024).

Synthesis of $[\text{Ni}(\text{OH}_2)_6]\text{Cl}_2 \cdot (18\text{-crown-6})_2 \cdot 2\text{H}_2\text{O}$. A scintillation vial was charged with 0.025 g (0.19 mmol, 1 eq.) of NiCl_2 to 0.105 g (0.386 mmol, 2 eq.) of 18-crown-6 ether in 10 mL of tetrahydrofuran or acetonitrile. The vial was heated to 353 K for 1.5 h and placed in a 277 K fridge to cool for 1 week. After 1 week, the cap was removed for slow evaporation over 5 days, resulting in a non-crystalline light-blue solid. The solid was taken into deionized water and light blue crystals suitable for X-ray diffraction were obtained after 2 months in a 277 K fridge and identified as $[\text{Ni}(\text{OH}_2)_6(18\text{-crown-6})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. ^1H NMR (CDCl_3 , 399.777 MHz): $\delta = 3.68$ (s, 4H, CH_2 -18-crown-6), 3.58 (s, 4H, $\text{H}_2\text{O}_{\text{eq}}-\text{Ni}$), 3.52 (s, 4H, $\text{H}_2\text{O}_{\text{eq}}-\text{Ni}$). ^{13}C NMR (CDCl_3 , 399.777 MHz): $\delta = 70.72$ (s, 18-crown-6). Analysis calculated for $\text{C}_{24}\text{H}_{64}\text{Cl}_2\text{Ni}_1\text{O}_{20}$: C, 35.93; H, 8.04; N, 0.00. Found: C, 35.97; H, 8.00; N, <0.10.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms attached to oxygen were freely refined, and those attached to carbon were refined using a riding model.

Funding information

Funding for this research was provided by: National Science Foundation, Directorate for Mathematical and Physical Sciences (award No. 1847926 to S. Chantal E. Stieber; award No. 1040566); Camille and Henry Dreyfus Foundation (award to S. Chantal E. Stieber); US Department of Defense, US Army (award No. W911NF-17-1-0537 to S. Chantal E. Stieber).

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Table 2

Experimental details.

Crystal data	
Chemical formula	$[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot 2\text{C}_{12}\text{H}_{24}\text{O}_6 \cdot 2\text{H}_2\text{O}$
M_r	401.18
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	105
a, b, c (Å)	7.6472 (2), 10.4180 (3), 12.7214 (3)
α, β, γ (°)	77.288 (1), 77.649 (1), 75.400 (1)
V (Å ³)	943.16 (4)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.73
Crystal size (mm)	0.3 × 0.2 × 0.15
Data collection	
Diffractometer	Bruker D8 Venture Kappa
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.708, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	57779, 4152, 4021
R_{int}	0.030
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.022, 0.056, 1.05
No. of reflections	4152
No. of parameters	243
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)	0.55, −0.27

Computer programs: *APEX4* and *SAINT* (Bruker, 2016), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2019/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

Acta Cryst. (2024). E80 [https://doi.org/10.1107/S2056989024010041]

Crystal structure of $[\text{Ni}(\text{OH}_2)_6]\text{Cl}_2 \cdot (18\text{-crown-6})_2 \cdot 2\text{H}_2\text{O}$

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Computing details

Hexaaquanickel(II) dichloride–1,4,7,10,13,16-hexaoxacyclooctadecane–water (1/2/2)

Crystal data

$[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot 2\text{C}_{12}\text{H}_{24}\text{O}_6 \cdot 2\text{H}_2\text{O}$

$M_r = 401.18$

Triclinic, $P\bar{1}$

$a = 7.6472$ (2) Å

$b = 10.4180$ (3) Å

$c = 12.7214$ (3) Å

$\alpha = 77.288$ (1)°

$\beta = 77.649$ (1)°

$\gamma = 75.400$ (1)°

$V = 943.16$ (4) Å³

$Z = 2$

$F(000) = 430$

$D_x = 1.413$ Mg m⁻³

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

Cell parameters from 401129 reflections

$\theta = 3.3\text{--}61.8^\circ$

$\mu = 0.73$ mm⁻¹

$T = 105$ K

Prism, blue

$0.3 \times 0.2 \times 0.15$ mm

Data collection

Bruker D8 Ventrue Kappa

diffractometer

φ and ω scans

Absorption correction: multi-scan

(SADABS; Krause et al. 2015)

$T_{\min} = 0.708$, $T_{\max} = 0.753$

57779 measured reflections

4152 independent reflections

4021 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 27.1^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -9 \rightarrow 9$

$k = -13 \rightarrow 13$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.056$

$S = 1.05$

4152 reflections

243 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 0.4776P]$

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

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

$\Delta\rho_{\max} = 0.55$ e Å⁻³

$\Delta\rho_{\min} = -0.27$ 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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.500000	0.500000	0.500000	0.00937 (6)
O1	0.74883 (11)	0.54896 (9)	0.47148 (7)	0.01664 (16)
H1C	0.821 (2)	0.5382 (17)	0.4171 (15)	0.030 (4)*
H1D	0.778 (2)	0.5951 (18)	0.5023 (14)	0.029 (4)*
O2	0.41319 (11)	0.65045 (8)	0.37574 (6)	0.01457 (15)
H2C	0.305 (2)	0.6640 (11)	0.3818 (7)	0.022*
H2D	0.444 (2)	0.7214 (19)	0.3595 (14)	0.033 (4)*
O3	0.40189 (11)	0.62253 (8)	0.61474 (7)	0.01512 (16)
H3C	0.408 (3)	0.700 (2)	0.5864 (9)	0.050 (6)*
H3D	0.405 (2)	0.6015 (17)	0.6772 (15)	0.030 (4)*
Cl1	0.47188 (4)	0.94579 (3)	0.31034 (2)	0.02239 (7)
O4	0.98032 (11)	0.51777 (8)	0.27500 (6)	0.01835 (17)
O5	1.04252 (11)	0.72559 (8)	0.36473 (6)	0.01574 (16)
O6	0.83961 (11)	0.71618 (8)	0.57969 (7)	0.01876 (17)
C1	1.04444 (16)	0.38560 (12)	0.24807 (10)	0.0199 (2)
H1A	1.082780	0.393417	0.167909	0.024*
H1B	0.942598	0.337326	0.269884	0.024*
C2	1.08752 (17)	0.61212 (12)	0.21450 (9)	0.0205 (2)
H2A	1.081962	0.625478	0.135692	0.025*
H2B	1.217120	0.577741	0.224260	0.025*
C3	1.01268 (17)	0.74326 (12)	0.25528 (9)	0.0209 (2)
H3A	1.074762	0.813511	0.208231	0.025*
H3B	0.879844	0.772696	0.252643	0.025*
C4	0.95456 (17)	0.84335 (11)	0.41173 (10)	0.0209 (2)
H4A	0.826966	0.874342	0.397501	0.025*
H4B	1.020641	0.916732	0.378365	0.025*
C5	0.95495 (17)	0.80970 (12)	0.53261 (10)	0.0214 (2)
H5A	1.081248	0.769581	0.547092	0.026*
H5B	0.908820	0.892442	0.565154	0.026*
C6	0.79639 (16)	0.69565 (12)	0.69632 (10)	0.0198 (2)
H6A	0.693210	0.648771	0.720440	0.024*
H6B	0.755295	0.784474	0.719885	0.024*
O7	0.36897 (11)	0.62695 (8)	0.84393 (6)	0.01766 (17)
O8	0.25973 (11)	0.31411 (8)	0.99165 (6)	0.01729 (16)
O9	−0.03393 (11)	0.18666 (8)	1.05124 (6)	0.01760 (16)
C7	0.35114 (16)	0.75844 (11)	0.86804 (9)	0.0179 (2)
H7A	0.447088	0.800913	0.817911	0.021*
H7B	0.374123	0.748131	0.943456	0.021*
C8	0.29069 (15)	0.53668 (11)	0.93233 (9)	0.0151 (2)
H8A	0.155630	0.567191	0.946136	0.018*
H8B	0.337591	0.534152	0.999674	0.018*
C9	0.34296 (15)	0.39801 (11)	0.90153 (9)	0.0154 (2)
H9A	0.296647	0.399490	0.834220	0.018*
H9B	0.477788	0.365714	0.889178	0.018*
C10	0.27876 (15)	0.18097 (11)	0.97362 (9)	0.0167 (2)

H10A	0.406193	0.129700	0.976358	0.020*
H10B	0.250080	0.183574	0.900792	0.020*
C11	0.14764 (15)	0.11431 (11)	1.06188 (9)	0.0170 (2)
H11A	0.162465	0.019455	1.054209	0.020*
H11B	0.173090	0.115194	1.134794	0.020*
C12	−0.16698 (16)	0.14810 (11)	1.14179 (9)	0.0174 (2)
H12A	−0.129468	0.151928	1.210664	0.021*
H12B	−0.175679	0.054352	1.143799	0.021*
O10	0.36399 (13)	0.88510 (9)	0.56722 (8)	0.02240 (18)
H10C	0.419 (3)	0.923 (2)	0.5967 (16)	0.041 (5)*
H10D	0.398 (3)	0.9071 (19)	0.4982 (17)	0.038 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.00966 (9)	0.00851 (9)	0.01044 (9)	−0.00317 (6)	−0.00040 (6)	−0.00254 (6)
O1	0.0145 (4)	0.0227 (4)	0.0167 (4)	−0.0104 (3)	0.0035 (3)	−0.0103 (3)
O2	0.0130 (4)	0.0122 (4)	0.0178 (4)	−0.0037 (3)	−0.0030 (3)	0.0002 (3)
O3	0.0218 (4)	0.0117 (4)	0.0116 (4)	−0.0040 (3)	−0.0014 (3)	−0.0025 (3)
Cl1	0.02783 (15)	0.01424 (13)	0.02534 (15)	−0.00744 (11)	−0.00474 (11)	−0.00032 (10)
O4	0.0194 (4)	0.0197 (4)	0.0153 (4)	−0.0040 (3)	0.0016 (3)	−0.0065 (3)
O5	0.0155 (4)	0.0136 (4)	0.0179 (4)	−0.0015 (3)	−0.0043 (3)	−0.0030 (3)
O6	0.0210 (4)	0.0196 (4)	0.0188 (4)	−0.0061 (3)	−0.0045 (3)	−0.0068 (3)
C1	0.0180 (5)	0.0260 (6)	0.0184 (5)	−0.0046 (4)	−0.0010 (4)	−0.0113 (5)
C2	0.0208 (6)	0.0239 (6)	0.0136 (5)	−0.0046 (5)	0.0028 (4)	−0.0021 (4)
C3	0.0258 (6)	0.0182 (5)	0.0151 (5)	−0.0031 (4)	−0.0032 (4)	0.0023 (4)
C4	0.0248 (6)	0.0120 (5)	0.0266 (6)	−0.0040 (4)	−0.0041 (5)	−0.0048 (4)
C5	0.0211 (6)	0.0214 (6)	0.0270 (6)	−0.0080 (5)	−0.0049 (5)	−0.0105 (5)
C6	0.0160 (5)	0.0234 (6)	0.0217 (6)	−0.0035 (4)	−0.0002 (4)	−0.0110 (5)
O7	0.0225 (4)	0.0152 (4)	0.0140 (4)	−0.0077 (3)	0.0035 (3)	−0.0023 (3)
O8	0.0224 (4)	0.0142 (4)	0.0143 (4)	−0.0067 (3)	0.0027 (3)	−0.0032 (3)
O9	0.0151 (4)	0.0186 (4)	0.0157 (4)	−0.0034 (3)	−0.0003 (3)	0.0015 (3)
C7	0.0180 (5)	0.0170 (5)	0.0198 (5)	−0.0081 (4)	0.0007 (4)	−0.0043 (4)
C8	0.0155 (5)	0.0165 (5)	0.0125 (5)	−0.0054 (4)	0.0000 (4)	−0.0006 (4)
C9	0.0153 (5)	0.0174 (5)	0.0126 (5)	−0.0050 (4)	0.0001 (4)	−0.0015 (4)
C10	0.0165 (5)	0.0141 (5)	0.0189 (5)	−0.0023 (4)	−0.0012 (4)	−0.0045 (4)
C11	0.0173 (5)	0.0130 (5)	0.0195 (5)	−0.0017 (4)	−0.0040 (4)	−0.0012 (4)
C12	0.0200 (5)	0.0161 (5)	0.0152 (5)	−0.0072 (4)	0.0005 (4)	−0.0006 (4)
O10	0.0265 (5)	0.0146 (4)	0.0268 (5)	−0.0077 (3)	−0.0014 (4)	−0.0044 (3)

Geometric parameters (Å, °)

Ni1—O1	2.0310 (8)	C4—C5	1.5007 (17)
Ni1—O1 ⁱ	2.0310 (8)	C5—H5A	0.9900
Ni1—O2	2.0567 (8)	C5—H5B	0.9900
Ni1—O2 ⁱ	2.0567 (8)	C6—H6A	0.9900
Ni1—O3	2.0474 (8)	C6—H6B	0.9900
Ni1—O3 ⁱ	2.0473 (8)	O7—C7	1.4359 (13)

O1—H1C	0.796 (19)	O7—C8	1.4275 (13)
O1—H1D	0.782 (19)	O8—C9	1.4179 (13)
O2—H2C	0.796 (18)	O8—C10	1.4218 (13)
O2—H2D	0.803 (19)	O9—C11	1.4221 (13)
O3—H3C	0.81 (2)	O9—C12	1.4229 (13)
O3—H3D	0.780 (19)	C7—H7A	0.9900
O4—C1	1.4314 (14)	C7—H7B	0.9900
O4—C2	1.4262 (14)	C7—C12 ⁱⁱⁱ	1.5091 (16)
O5—C3	1.4236 (14)	C8—H8A	0.9900
O5—C4	1.4317 (13)	C8—H8B	0.9900
O6—C5	1.4270 (14)	C8—C9	1.5137 (15)
O6—C6	1.4292 (14)	C9—H9A	0.9900
C1—H1A	0.9900	C9—H9B	0.9900
C1—H1B	0.9900	C10—H10A	0.9900
C1—C6 ⁱⁱ	1.5113 (17)	C10—H10B	0.9900
C2—H2A	0.9900	C10—C11	1.5082 (15)
C2—H2B	0.9900	C11—H11A	0.9900
C2—C3	1.5013 (17)	C11—H11B	0.9900
C3—H3A	0.9900	C12—H12A	0.9900
C3—H3B	0.9900	C12—H12B	0.9900
C4—H4A	0.9900	O10—H10C	0.83 (2)
C4—H4B	0.9900	O10—H10D	0.86 (2)
O1—Ni1—O1 ⁱ	180.0	O6—C5—H5A	110.0
O1—Ni1—O2 ⁱ	88.38 (3)	O6—C5—H5B	110.0
O1 ⁱ —Ni1—O2 ⁱ	91.62 (3)	C4—C5—H5A	110.0
O1—Ni1—O2	91.62 (3)	C4—C5—H5B	110.0
O1 ⁱ —Ni1—O2	88.38 (3)	H5A—C5—H5B	108.4
O1—Ni1—O3 ⁱ	88.95 (3)	O6—C6—C1 ⁱⁱ	113.46 (9)
O1—Ni1—O3	91.05 (3)	O6—C6—H6A	108.9
O1 ⁱ —Ni1—O3 ⁱ	91.05 (3)	O6—C6—H6B	108.9
O1 ⁱ —Ni1—O3	88.95 (3)	C1 ⁱⁱ —C6—H6A	108.9
O2—Ni1—O2 ⁱ	180.0	C1 ⁱⁱ —C6—H6B	108.9
O3—Ni1—O2 ⁱ	87.10 (3)	H6A—C6—H6B	107.7
O3 ⁱ —Ni1—O2	87.10 (3)	C8—O7—C7	113.97 (8)
O3—Ni1—O2	92.90 (3)	C9—O8—C10	113.64 (8)
O3 ⁱ —Ni1—O2 ⁱ	92.90 (3)	C11—O9—C12	113.03 (8)
O3 ⁱ —Ni1—O3	180.0	O7—C7—H7A	108.6
Ni1—O1—H1C	122.3 (12)	O7—C7—H7B	108.6
Ni1—O1—H1D	126.2 (13)	O7—C7—C12 ⁱⁱⁱ	114.74 (9)
H1C—O1—H1D	109.8 (17)	H7A—C7—H7B	107.6
Ni1—O2—H2C	109.5	C12 ⁱⁱⁱ —C7—H7A	108.6
Ni1—O2—H2D	123.9 (13)	C12 ⁱⁱⁱ —C7—H7B	108.6
H2C—O2—H2D	108.9	O7—C8—H8A	110.1
Ni1—O3—H3C	109.5	O7—C8—H8B	110.1
Ni1—O3—H3D	126.3 (13)	O7—C8—C9	108.12 (8)
H3C—O3—H3D	117.7	H8A—C8—H8B	108.4
C2—O4—C1	114.07 (9)	C9—C8—H8A	110.1

C3—O5—C4	111.15 (9)	C9—C8—H8B	110.1
C5—O6—C6	114.59 (9)	O8—C9—C8	105.27 (8)
O4—C1—H1A	109.1	O8—C9—H9A	110.7
O4—C1—H1B	109.1	O8—C9—H9B	110.7
O4—C1—C6 ⁱⁱ	112.49 (9)	C8—C9—H9A	110.7
H1A—C1—H1B	107.8	C8—C9—H9B	110.7
C6 ⁱⁱ —C1—H1A	109.1	H9A—C9—H9B	108.8
C6 ⁱⁱ —C1—H1B	109.1	O8—C10—H10A	110.1
O4—C2—H2A	110.0	O8—C10—H10B	110.1
O4—C2—H2B	110.0	O8—C10—C11	107.97 (9)
O4—C2—C3	108.55 (9)	H10A—C10—H10B	108.4
H2A—C2—H2B	108.4	C11—C10—H10A	110.1
C3—C2—H2A	110.0	C11—C10—H10B	110.1
C3—C2—H2B	110.0	O9—C11—C10	108.25 (9)
O5—C3—C2	109.06 (9)	O9—C11—H11A	110.0
O5—C3—H3A	109.9	O9—C11—H11B	110.0
O5—C3—H3B	109.9	C10—C11—H11A	110.0
C2—C3—H3A	109.9	C10—C11—H11B	110.0
C2—C3—H3B	109.9	H11A—C11—H11B	108.4
H3A—C3—H3B	108.3	O9—C12—C7 ⁱⁱⁱ	109.84 (9)
O5—C4—H4A	109.9	O9—C12—H12A	109.7
O5—C4—H4B	109.9	O9—C12—H12B	109.7
O5—C4—C5	108.90 (9)	C7 ⁱⁱⁱ —C12—H12A	109.7
H4A—C4—H4B	108.3	C7 ⁱⁱⁱ —C12—H12B	109.7
C5—C4—H4A	109.9	H12A—C12—H12B	108.2
C5—C4—H4B	109.9	H10C—O10—H10D	105.9 (18)
O6—C5—C4	108.27 (9)		
O4—C2—C3—O5	66.72 (12)	O7—C8—C9—O8	−179.36 (8)
O5—C4—C5—O6	−66.75 (12)	O8—C10—C11—O9	62.92 (11)
C1—O4—C2—C3	−176.61 (9)	C7—O7—C8—C9	−172.00 (9)
C2—O4—C1—C6 ⁱⁱ	80.37 (12)	C8—O7—C7—C12 ⁱⁱⁱ	−80.86 (12)
C3—O5—C4—C5	167.84 (9)	C9—O8—C10—C11	−166.27 (9)
C4—O5—C3—C2	−173.18 (9)	C10—O8—C9—C8	174.26 (9)
C5—O6—C6—C1 ⁱⁱ	−72.73 (12)	C11—O9—C12—C7 ⁱⁱⁱ	172.32 (9)
C6—O6—C5—C4	−167.84 (9)	C12—O9—C11—C10	−169.24 (9)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1C $\cdots$ O4	0.797 (18)	1.973 (18)	2.7679 (12)	174.7 (17)
O1—H1D $\cdots$ O6	0.780 (18)	1.956 (18)	2.7360 (12)	177.3 (17)
O2—H2C $\cdots$ O5 ^{iv}	0.79 (2)	1.99 (2)	2.7695 (12)	167 (1)
O2—H2D $\cdots$ C11	0.803 (19)	2.335 (19)	3.1258 (9)	168.6 (16)
O3—H3C $\cdots$ O10	0.82 (2)	1.84 (2)	2.6229 (12)	160 (2)
O3—H3D $\cdots$ O7	0.780 (18)	2.146 (18)	2.8819 (11)	157.4 (17)

O10—H10C $\cdots$ C11 ^v	0.83 (2)	2.38 (2)	3.2038 (10)	171 (2)
O10—H10D $\cdots$ C11	0.86 (2)	2.30 (2)	3.1559 (10)	173 (2)

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