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Crystal structure of hexaaquanickel(II) bis{2-[(5,6-dihydroxy-3-sulfonatoquinolin-1-ium-7-yl)oxy]-acetate} dihydrate

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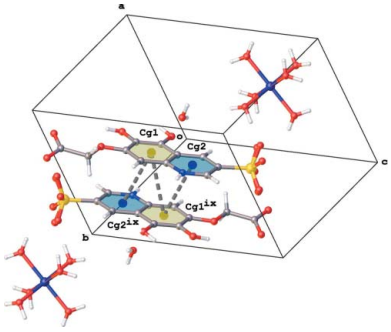
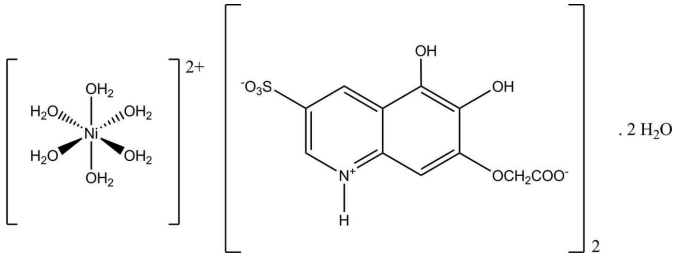
The asymmetric unit of the title compound, $[Ni(H_2O)_6](C_{11}H_8NO_8S)_2\cdot 2H_2O$, features a half-hexaaquanickel(II) complex cation with the Ni^{II} ion on an inversion center, one deprotonated 5,6-dihydroxy-3-sulfoquinolin-7-yloxyacetic acid (**QOH**) molecule appearing in its zwitterionic form and one lattice water molecule. The sulfonate group is disordered over two positions with occupancy factors of 0.655 (5) and 0.345 (5). The hexaaquanickel(II) cation interacts through hydrogen bonding with eight **QOH** molecules and two water molecules. The six-membered rings of quinoline show π–π stacking [centroid-to-centroid distances of 3.679 (2) Å and 3.714 (2) Å].

1. Chemical context

Quinoline and its derivatives have been of great interest due to their interesting biochemical activities. Quinine, cinchonine, chloroquine, plasmoquine and acriquine, for instance, are known to be able to cure malaria (Foley & Tilley, 1998; Długosz & Duś, 1996; Nayyar *et al.*, 2006). Complexes of quinoline-containing organic compounds with transition metals are also known for their wide variety of structures and profound biochemical activities which allow them to act as antibacterial and anti-Alzheimer agents (Deraeve *et al.*, 2008) and as cures for many types of cancers such as cervical cancer, lung cancer and breast cancer (Yan *et al.*, 2012; Daniel *et al.*, 2004). These complexes, therefore, have been synthesized and investigated intensively (Kitanovic *et al.*, 2014).





Recently, the new quinoline derivative 6-hydroxy-3-sulfoquinolin-7-yloxyacetic (**Q**) has been synthesized from eugenol and its antibacterial activities have been reported (Dinh *et al.*, 2012). Here, we report the synthesis of 5,6-dihydroxy-3-sulfoquinolin-7-yloxyacetic acid (**QOH**). As quinoline rings are known to complex with metal ions, the formation of a complex between **QOH** and Ni^{II} was studied. The reaction product, however, could not be characterized unambiguously

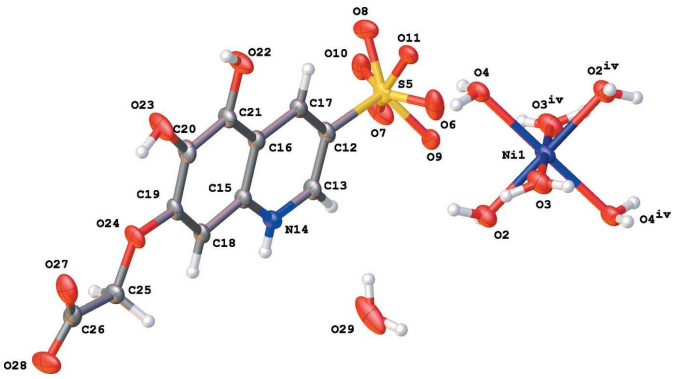


Figure 1
The structures of the molecular components in the title compound with ellipsoids drawn at the 50% probability level. [Symmetry code: (iv) $-x+2$, $-y+1$, $-z+2$.]

by IR or ^{1}H NMR spectroscopic methods. The spectroscopic data are different from those obtained for free **QOH** and in favour of a deprotonated carboxylic acid group, but give no indication about a possible complex formation. X-ray diffraction now shows that **QOH** is not complexing directly with Ni^{II}.

2. Structural commentary

The structure determination shows that the carboxyl group of **QOH** is deprotonated and the anion is present in its zwitterionic form (Fig. 1), which was also observed for **Q** (Dinh *et al.*, 2012). The best plane through the quinoline ring (r.m.s. deviation = 0.009 Å) makes an angle of 15.29 (19)° with the carboxylate plane. The sulfonate group at the 3-position occurs in two orientations with occupancy factors of 0.655 (5) and 0.345 (5). **QOH**, however, is not acting as a ligand for Ni^{II}, which occurs as a hexaaqua complex. This $[Ni(H_2O)_6]^{2+}$ is located about an inversion center and has an octahedral volume of 11.629 Å^3 with Ni—O bond lengths between 2.034 (3) and 2.106 (2) Å.

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···O27^{i}	0.84	1.86	2.694 (3)	175
O2—H2B···O29^{ii}	0.88 (4)	1.85 (4)	2.718 (5)	169 (4)
O3—H3A···O8^{iii}	0.84	2.14	2.829 (5)	139
O3—H3B···O6^{iv}	0.76 (5)	2.05 (5)	2.691 (5)	142 (5)
O4—H4A···O28^{i}	0.84	1.73	2.569 (4)	173
O4—H4B···O6	0.81 (4)	1.95 (4)	2.709 (5)	156 (4)
N14—H14···O4^{v}	0.81 (4)	2.00 (4)	2.809 (4)	174 (3)
O22—H22···O8^{vi}	0.84	2.03	2.779 (5)	147
O23—H23···O29^{i}	0.84	1.85	2.625 (5)	153
O29—H29A···O27^{i}	0.83 (4)	1.82 (4)	2.630 (4)	165 (4)
O29—H29B···O7^{iii}	0.83 (4)	2.23 (4)	2.959 (6)	148 (5)
C13—H13···O7^{vii}	0.95	2.24	3.166 (6)	165
C17—H17···O22^{vi}	0.95	2.43	3.354 (4)	166
C18—H18···O28^{viii}	0.95	2.40	3.345 (5)	176

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

3. Supramolecular features

The hexaaquanickel(II) cation plays the role of glue in the crystal packing. In total, it interacts with eight **QOH** moieties and two water molecules through O—H···O and N—H···O hydrogen bonding (Table 1, Fig. 2).

Furthermore, π–π stacking between the quinoline rings results in the formation of inversion dimers [$Cg1\cdots Cg1^{ix}$ = 3.679 (2) Å, $Cg1\cdots Cg2^{ix}$ = 3.714 (2) Å; $Cg1$ and $Cg2$ are the centroids of the rings C12/C13/N14/C15–C17 and C15/C16/C18–C21, respectively; symmetry code: (ix) $-x+1, -y+2, -z+1$; Fig. 3].

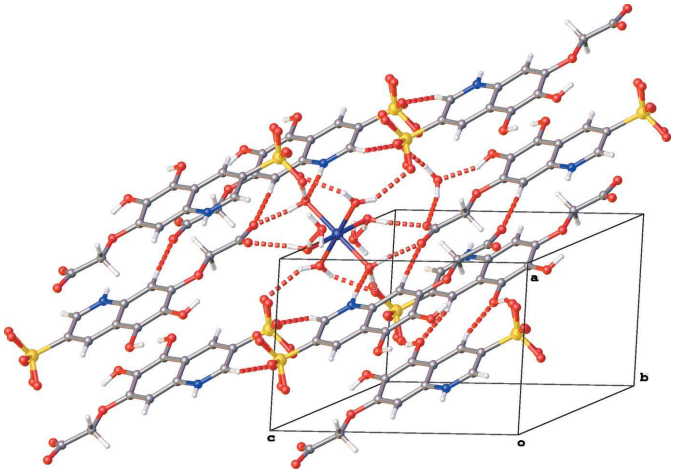


Figure 2
Partial packing diagram of the title compound, showing the hydrogen-bonding interactions (red dotted lines, see Table 1 for details).

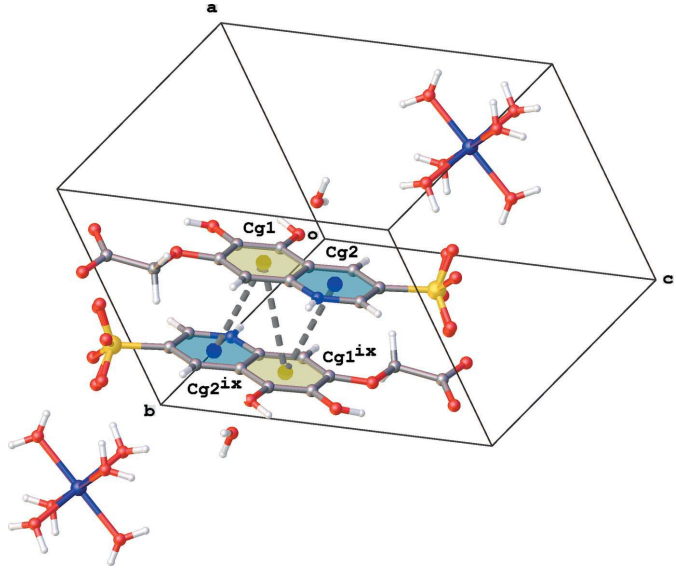


Figure 3
Partial packing diagram of the title compound, showing π–π interactions between quinoline rings (grey dotted lines; $Cg1$ and $Cg2$ are the centroids of rings C12/C13/N14/C15–C17 and C15/C16/C18–C21, respectively). [Symmetry code: (ix) $-x+1, -y+2, -z+1$.]

Lattice water molecule O29 interacts with the carboxylate (O27) and hydroxyl (O23) groups of a neighboring **QOH** molecule and furthermore with the sulfonate group (O7) of a second **QOH** molecule and the hexaaqua complex (O2). Whereas hydroxyl group O23—H23 only interacts with water molecule O29, the second hydroxyl group O22—H22 is involved in the formation of another type of inversion dimers through C—H···O hydrogen bonding and interacts with a sulfonate group (O8) (Table 1, Fig. 2).

4. Database survey

A search of the Cambridge Structural Database (Version 5.36; last update May 2015; Groom & Allen, 2014) for quinoline derivatives gives 3040 hits of which 529 are protonated at the nitrogen atom. Searching for quinoline derivatives bearing a sulfonate group results in 30 hits for substitution at the 5-position, 3 hits at the 8-position, 2 hits at the 7-position and two structures have a sulfonate group at the 3-position [CSD refcodes BAPBOK (Skrzypek & Suwinska, 2002) and HIVHUQ (Skrzypek & Suwinska, 2007)]. As for the title compound, these two structures occur in the zwitterionic form, but do not show disorder in the sulfonate group.

5. Synthesis and crystallization

Starting from eugenol, a main constituent of *Ocimum sanctum L.* oil, the quinoline derivative 6-hydroxy-3-sulfoquinolin-7-yloxyacetic acid (**Q**) was synthesized and further transformed to 5,6-dihydroxy-3-sulfoquinolin-7-yloxyacetic acid (**QOH**) according to a procedure described by Dinh *et al.* (2012).

A solution containing $NiCl_2{\cdot}6H_2O$ (0.262 g, 1.1 mmol) in ethanol–water (10 mL; 1:1 *v*/*v*) was added dropwise to a solution of **QOH** (0.630 g, 2 mmol) in ethanol–water (15 mL, 1:1 *v*/*v*). The obtained solution was stirred for three hours, at 313–323 K, during reflux. A few days later, the green–yellow precipitate was collected by filtration, washed consecutively with ethanol and diethyl ether and dried *in vacuo*. The obtained crystals are soluble in water and DMSO, but only slightly soluble in ethanol, acetone and chloroform. The yield was 65%. Single crystals suitable for X-ray investigation were obtained by slow evaporation from a ethanol–water (1:1 *v*/*v*) solution at room temperature. IR (Impack-410 Nicolet spectrometer, KBr, cm^{-1}): 3420 (ν_{OH}); 3080, 2918 ($\nu_{C\text{-}H}$); 1620 (ν_{COOas}); 1426(ν_{COOs}); 1528 ($\nu_{C=Cring}$ or $\nu_{C=N}$); 466 ($\nu_{Ni\text{-}O}$). ^{1}H NMR (Bruker Avance 500 MHz, d_6-DMSO): δ 8.74 (1H, *s*, Ar), 8.17 (1H, *s*, Ar), 7.2 (1H, *s*, Ar), 4.64 (2H, *s*, CH_2); (Bruker Avance 500 MHz, D_2O): δ 9.26 (1H, *s*, Ar), 9.01 (1H, *s*, Ar), 7.01 (1H, *s*, Ar), 4.80 (2H, *s*, CH_2).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms H2*B*, H3*B*, H4*B*, H14, H29*A* and H29*B* were located in difference Fourier maps. All other H atoms were placed at idealized positions and refined in riding mode, with C—H distances of 0.95 (aromatic) and 0.99 Å (methylene), and O—H distances of 0.84 Å. The H atoms of water molecule O29 were refined with an O—H distance restraint of 0.85 Å and H···H distance restraint of 1.39 Å. For all H atoms, U_{iso}(H) values were assigned as $1.2U_{eq}$ of the parent atoms ($1.5U_{eq}$ for H22 and H23). The SO_3 group is disordered over two positions, the occupancy ratio refines to 0.655 (5):0.345 (5) for part 1 (O6, O7, 08) and part 2 (O9, O10, O11), respectively.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ni(H_2O)_6](C_{11}H_8NO_8S)_2{\cdot}2H_2O$
M_r	831.31
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, *b*, *c* (Å)	8.1632 (5), 8.2829 (6), 11.8492 (8)
α, β, γ (°)	102.316 (6), 102.250 (6), 93.003 (6)
V (Å^3)	760.91 (9)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.88
Crystal size (mm)	0.3 × 0.2 × 0.15
Data collection	
Diffractometer	Agilent SuperNova (single source at offset, Eos detector)
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2012)
T_{min}, T_{max}	0.781, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8135, 3071, 2513
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.125, 1.09
No. of reflections	3071
No. of parameters	283
No. of restraints	213
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.84

Computer programs: *CrysAlis PRO* (Agilent, 2012), *XS* and *SHELXL* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

Acknowledgements

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: *XS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2008); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

Hexaaquanickel(II) bis(5,6-dihydroxy-3-sulfoquinolin-7-yloxyacetic acid) dihydrate

Crystal data

$[Ni(H_2O)_6](C_{11}H_8NO_8S)_2\cdot 2H_2O$
$M_r = 831.31$
Triclinic, $P\overline{1}$
$a = 8.1632$ (5) Å
$b = 8.2829$ (6) Å
$c = 11.8492$ (8) Å
$\alpha = 102.316$ (6)°
$\beta = 102.250$ (6)°
$\gamma = 93.003$ (6)°
$V = 760.91$ (9) Å^3
$Z = 1$
$F(000) = 430$
$D_x = 1.814$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2769 reflections
$\theta = 3.4$–$28.9°$
$\mu = 0.88$ mm^{-1}
$T = 100$ K
Block, yellow
0.3 × 0.2 × 0.15 mm

Data collection

Agilent SuperNova (single source at offset, Eos detector) diffractometer
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 15.9631 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)
$T_{min} = 0.781$, $T_{max} = 1.000$
8135 measured reflections
3071 independent reflections
2513 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 26.4°$, $\theta_{min} = 2.8°$
$h = -10\rightarrow10$
$k = -10\rightarrow10$
$l = -14\rightarrow14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.125$
$S = 1.09$
3071 reflections
283 parameters
213 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 1.8778P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.84$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	1.0000	0.5000	1.0000	0.02176 (19)	
O2	1.0198 (3)	0.7442 (3)	0.9941 (2)	0.0260 (6)	
H2A	0.9996	0.7520	0.9230	0.031*	
H2B	0.952 (5)	0.803 (5)	1.031 (4)	0.031*	
O3	1.1954 (4)	0.4632 (3)	0.9188 (2)	0.0313 (6)	
H3A	1.1967	0.5296	0.8744	0.038*	
H3B	1.265 (6)	0.413 (6)	0.943 (4)	0.038*	
O4	0.8307 (3)	0.4307 (3)	0.8328 (2)	0.0249 (5)	
H4A	0.8770	0.4558	0.7811	0.030*	
H4B	0.748 (5)	0.478 (5)	0.840 (4)	0.030*	
S5	0.48964 (11)	0.73394 (10)	0.85461 (7)	0.0223 (2)	
O6	0.6221 (5)	0.6546 (6)	0.9048 (4)	0.0389 (13)	0.655 (5)
O7	0.4212 (6)	0.8513 (5)	0.9337 (4)	0.0368 (12)	0.655 (5)
O8	0.3539 (5)	0.6107 (5)	0.7699 (3)	0.0321 (11)	0.655 (5)
O9	0.6135 (9)	0.7895 (10)	0.9785 (6)	0.029 (2)	0.345 (5)
O10	0.3282 (9)	0.7681 (11)	0.8587 (7)	0.031 (2)	0.345 (5)
O11	0.5153 (9)	0.5620 (9)	0.8093 (6)	0.0245 (18)	0.345 (5)
C12	0.5705 (4)	0.8478 (4)	0.7634 (3)	0.0213 (7)	
C13	0.6412 (4)	1.0124 (4)	0.8098 (3)	0.0213 (7)	
H13	0.6409	1.0658	0.8891	0.026*	
N14	0.7090 (4)	1.0941 (4)	0.7428 (2)	0.0212 (6)	
H14	0.744 (5)	1.190 (5)	0.774 (3)	0.025*	
C15	0.7152 (4)	1.0268 (4)	0.6280 (3)	0.0196 (7)	
C16	0.6429 (4)	0.8599 (4)	0.5784 (3)	0.0201 (7)	
C17	0.5717 (4)	0.7727 (4)	0.6481 (3)	0.0208 (7)	
H17	0.5240	0.6610	0.6158	0.025*	
C18	0.7910 (4)	1.1199 (4)	0.5627 (3)	0.0210 (7)	
H18	0.8376	1.2317	0.5962	0.025*	
C19	0.7951 (4)	1.0426 (4)	0.4485 (3)	0.0209 (7)	
C20	0.7240 (5)	0.8766 (4)	0.3960 (3)	0.0240 (7)	
C21	0.6498 (4)	0.7865 (4)	0.4600 (3)	0.0231 (7)	
O22	0.5812 (4)	0.6280 (3)	0.4145 (2)	0.0337 (6)	
H22	0.6086	0.5913	0.3501	0.051*	
O23	0.7252 (4)	0.7973 (3)	0.2843 (2)	0.0374 (7)	
H23	0.7859	0.8556	0.2560	0.056*	
O24	0.8641 (3)	1.1125 (3)	0.3741 (2)	0.0254 (5)	

C25	0.9285 (4)	1.2848 (4)	0.4117 (3)	0.0242 (7)
H25A	1.0146	1.3044	0.4872	0.029*
H25B	0.8362	1.3544	0.4246	0.029*
C26	1.0064 (4)	1.3300 (5)	0.3152 (3)	0.0271 (8)
O27	1.0256 (3)	1.2204 (3)	0.2309 (2)	0.0341 (6)
O28	1.0496 (4)	1.4828 (4)	0.3317 (2)	0.0424 (8)
O29	1.1564 (6)	1.0664 (4)	0.8667 (3)	0.0543 (10)
H29A	1.088 (5)	0.986 (5)	0.829 (4)	0.065*
H29B	1.242 (4)	1.041 (6)	0.908 (4)	0.065*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0296 (4)	0.0192 (3)	0.0192 (3)	−0.0028 (2)	0.0124 (3)	0.0049 (2)
O2	0.0364 (15)	0.0224 (12)	0.0229 (13)	0.0015 (11)	0.0139 (11)	0.0064 (10)
O3	0.0401 (16)	0.0279 (14)	0.0321 (15)	−0.0007 (11)	0.0206 (13)	0.0089 (11)
O4	0.0304 (14)	0.0262 (13)	0.0218 (12)	−0.0041 (10)	0.0120 (11)	0.0091 (10)
S5	0.0271 (5)	0.0246 (4)	0.0205 (4)	−0.0015 (3)	0.0129 (3)	0.0105 (3)
O6	0.030 (2)	0.059 (3)	0.043 (3)	0.008 (2)	0.0156 (19)	0.036 (2)
O7	0.061 (3)	0.030 (2)	0.031 (2)	0.004 (2)	0.034 (2)	0.0087 (18)
O8	0.037 (2)	0.039 (2)	0.0203 (19)	−0.0153 (18)	0.0114 (16)	0.0079 (16)
O9	0.030 (4)	0.039 (4)	0.020 (3)	−0.011 (3)	0.004 (3)	0.018 (3)
O10	0.021 (3)	0.048 (5)	0.036 (5)	0.004 (3)	0.012 (3)	0.027 (4)
O11	0.029 (4)	0.026 (3)	0.021 (4)	−0.007 (3)	0.007 (3)	0.011 (3)
C12	0.0217 (16)	0.0264 (16)	0.0218 (16)	0.0010 (13)	0.0103 (13)	0.0134 (13)
C13	0.0234 (17)	0.0279 (17)	0.0168 (15)	0.0005 (13)	0.0095 (13)	0.0100 (13)
N14	0.0248 (15)	0.0224 (14)	0.0181 (14)	−0.0035 (12)	0.0079 (11)	0.0065 (11)
C15	0.0195 (16)	0.0250 (16)	0.0176 (15)	0.0006 (13)	0.0072 (12)	0.0096 (12)
C16	0.0199 (16)	0.0255 (16)	0.0177 (15)	0.0013 (13)	0.0066 (12)	0.0090 (13)
C17	0.0203 (16)	0.0243 (16)	0.0206 (16)	−0.0007 (13)	0.0066 (13)	0.0100 (13)
C18	0.0208 (16)	0.0268 (17)	0.0193 (15)	−0.0012 (13)	0.0067 (13)	0.0125 (13)
C19	0.0218 (16)	0.0251 (16)	0.0227 (16)	0.0039 (13)	0.0110 (13)	0.0144 (13)
C20	0.0330 (19)	0.0274 (17)	0.0165 (15)	0.0046 (14)	0.0114 (14)	0.0093 (13)
C21	0.0301 (18)	0.0247 (16)	0.0173 (15)	−0.0015 (14)	0.0085 (13)	0.0086 (13)
O22	0.0572 (18)	0.0255 (13)	0.0210 (13)	−0.0090 (12)	0.0187 (12)	0.0044 (10)
O23	0.072 (2)	0.0257 (13)	0.0224 (13)	−0.0002 (13)	0.0269 (13)	0.0076 (11)
O24	0.0367 (14)	0.0249 (12)	0.0214 (12)	0.0000 (10)	0.0168 (10)	0.0108 (10)
C25	0.0257 (18)	0.0297 (18)	0.0201 (16)	−0.0045 (14)	0.0080 (14)	0.0110 (14)
C26	0.0219 (17)	0.041 (2)	0.0224 (17)	−0.0031 (15)	0.0059 (14)	0.0172 (15)
O27	0.0420 (16)	0.0423 (15)	0.0316 (14)	0.0108 (12)	0.0238 (12)	0.0211 (12)
O28	0.0592 (19)	0.0433 (16)	0.0254 (14)	−0.0226 (14)	0.0169 (13)	0.0088 (12)
O29	0.113 (3)	0.0303 (16)	0.0419 (19)	0.0166 (17)	0.057 (2)	0.0147 (14)

Geometric parameters (Å, º)

Ni1—O2	2.038 (2)	N14—C15	1.368 (4)
Ni1—O2^{i}	2.038 (2)	C15—C16	1.423 (5)
Ni1—O3^{i}	2.034 (3)	C15—C18	1.409 (4)

Ni1—O3	2.034 (3)	C16—C17	1.399 (4)
Ni1—O4^{i}	2.106 (2)	C16—C21	1.419 (5)
Ni1—O4	2.106 (2)	C17—H17	0.9500
O2—H2A	0.8400	C18—H18	0.9500
O2—H2B	0.88 (4)	C18—C19	1.375 (5)
O3—H3A	0.8400	C19—C20	1.419 (5)
O3—H3B	0.76 (5)	C19—O24	1.351 (4)
O4—H4A	0.8400	C20—C21	1.374 (4)
O4—H4B	0.81 (4)	C20—O23	1.348 (4)
S5—O6	1.387 (4)	C21—O22	1.350 (4)
S5—O7	1.423 (4)	O22—H22	0.8400
S5—O8	1.500 (4)	O23—H23	0.8400
S5—O9	1.556 (7)	O24—C25	1.436 (4)
S5—O10	1.371 (7)	C25—H25A	0.9900
S5—O11	1.454 (7)	C25—H25B	0.9900
S5—C12	1.779 (3)	C25—C26	1.522 (4)
C12—C13	1.399 (5)	C26—O27	1.242 (5)
C12—C17	1.377 (5)	C26—O28	1.258 (5)
C13—H13	0.9500	O29—H29A	0.827 (19)
C13—N14	1.331 (4)	O29—H29B	0.826 (19)
N14—H14	0.81 (4)		

O2^{i}—Ni1—O2	180.0	N14—C13—C12	119.9 (3)
O2—Ni1—O4	92.67 (10)	N14—C13—H13	120.0
O2^{i}—Ni1—O4^{i}	92.67 (10)	C13—N14—H14	115 (3)
O2^{i}—Ni1—O4	87.33 (10)	C13—N14—C15	123.9 (3)
O2—Ni1—O4^{i}	87.33 (10)	C15—N14—H14	121 (3)
O3^{i}—Ni1—O2	90.14 (11)	N14—C15—C16	117.3 (3)
O3—Ni1—O2	89.86 (11)	N14—C15—C18	120.9 (3)
O3^{i}—Ni1—O2^{i}	89.86 (11)	C18—C15—C16	121.9 (3)
O3—Ni1—O2^{i}	90.14 (11)	C17—C16—C15	119.3 (3)
O3^{i}—Ni1—O3	180.0	C17—C16—C21	122.3 (3)
O3—Ni1—O4^{i}	90.58 (11)	C21—C16—C15	118.3 (3)
O3^{i}—Ni1—O4^{i}	89.43 (11)	C12—C17—C16	120.4 (3)
O3—Ni1—O4	89.42 (11)	C12—C17—H17	119.8
O3^{i}—Ni1—O4	90.57 (11)	C16—C17—H17	119.8
O4^{i}—Ni1—O4	180.0	C15—C18—H18	121.3
Ni1—O2—H2A	109.5	C19—C18—C15	117.5 (3)
Ni1—O2—H2B	113 (3)	C19—C18—H18	121.3
H2A—O2—H2B	109.2	C18—C19—C20	122.2 (3)
Ni1—O3—H3A	109.5	O24—C19—C18	125.3 (3)
Ni1—O3—H3B	119 (4)	O24—C19—C20	112.4 (3)
H3A—O3—H3B	129.1	C21—C20—C19	120.0 (3)
Ni1—O4—H4A	109.5	O23—C20—C19	123.8 (3)
Ni1—O4—H4B	106 (3)	O23—C20—C21	116.2 (3)
H4A—O4—H4B	113.9	C20—C21—C16	120.1 (3)
O6—S5—O7	117.0 (3)	O22—C21—C16	117.5 (3)
O6—S5—O8	111.0 (3)	O22—C21—C20	122.4 (3)

O6—S5—C12	106.2 (2)	C21—O22—H22	109.5
O7—S5—O8	111.2 (3)	C20—O23—H23	109.5
O7—S5—C12	105.9 (2)	C19—O24—C25	118.6 (3)
O8—S5—C12	104.47 (18)	O24—C25—H25A	110.1
O9—S5—C12	104.9 (3)	O24—C25—H25B	110.1
O10—S5—O9	112.3 (5)	O24—C25—C26	108.1 (3)
O10—S5—O11	117.2 (5)	H25A—C25—H25B	108.4
O10—S5—C12	110.5 (3)	C26—C25—H25A	110.1
O11—S5—O9	105.7 (4)	C26—C25—H25B	110.1
O11—S5—C12	105.3 (3)	O27—C26—C25	120.6 (3)
C13—C12—S5	120.3 (2)	O27—C26—O28	125.5 (3)
C17—C12—S5	120.4 (3)	O28—C26—C25	113.9 (3)
C17—C12—C13	119.2 (3)	H29A—O29—H29B	114 (3)
C12—C13—H13	120.0		

S5—C12—C13—N14	176.7 (3)	C15—C16—C21—O22	179.8 (3)
S5—C12—C17—C16	−176.8 (3)	C15—C18—C19—C20	1.0 (5)
O6—S5—C12—C13	−90.9 (4)	C15—C18—C19—O24	−179.3 (3)
O6—S5—C12—C17	85.9 (4)	C16—C15—C18—C19	−0.9 (5)
O7—S5—C12—C13	34.2 (4)	C17—C12—C13—N14	−0.2 (5)
O7—S5—C12—C17	−149.0 (3)	C17—C16—C21—C20	−178.7 (3)
O8—S5—C12—C13	151.7 (3)	C17—C16—C21—O22	1.5 (5)
O8—S5—C12—C17	−31.5 (4)	C18—C15—C16—C17	179.0 (3)
O9—S5—C12—C13	−37.7 (4)	C18—C15—C16—C21	0.6 (5)
O9—S5—C12—C17	139.1 (4)	C18—C19—C20—C21	−0.9 (5)
O10—S5—C12—C13	83.5 (5)	C18—C19—C20—O23	179.7 (3)
O10—S5—C12—C17	−99.7 (5)	C18—C19—O24—C25	−4.8 (5)
O11—S5—C12—C13	−149.1 (4)	C19—C20—C21—C16	0.6 (5)
O11—S5—C12—C17	27.7 (4)	C19—C20—C21—O22	−179.6 (3)
C12—C13—N14—C15	−0.2 (5)	C19—O24—C25—C26	177.2 (3)
C13—C12—C17—C16	0.0 (5)	C20—C19—O24—C25	174.9 (3)
C13—N14—C15—C16	0.6 (5)	C21—C16—C17—C12	178.8 (3)
C13—N14—C15—C18	−179.1 (3)	O23—C20—C21—C16	180.0 (3)
N14—C15—C16—C17	−0.8 (5)	O23—C20—C21—O22	−0.2 (5)
N14—C15—C16—C21	−179.2 (3)	O24—C19—C20—C21	179.4 (3)
N14—C15—C18—C19	178.9 (3)	O24—C19—C20—O23	0.0 (5)
C15—C16—C17—C12	0.5 (5)	O24—C25—C26—O27	−9.2 (5)
C15—C16—C21—C20	−0.4 (5)	O24—C25—C26—O28	172.1 (3)

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O27^{ii}	0.84	1.86	2.694 (3)	175
O2—H2*B*···O29^{iii}	0.88 (4)	1.85 (4)	2.718 (5)	169 (4)
O3—H3*A*···O8^{iv}	0.84	2.14	2.829 (5)	139
O3—H3*B*···O6^{i}	0.76 (5)	2.05 (5)	2.691 (5)	142 (5)

O4—H4*A*···O28^{ii}	0.84	1.73	2.569 (4)	173
O4—H4*B*···O6	0.81 (4)	1.95 (4)	2.709 (5)	156 (4)
N14—H14···O4^{v}	0.81 (4)	2.00 (4)	2.809 (4)	174 (3)
O22—H22···O8^{vi}	0.84	2.03	2.779 (5)	147
O23—H23···O29^{ii}	0.84	1.85	2.625 (5)	153
O29—H29*A*···O27^{ii}	0.83 (4)	1.82 (4)	2.630 (4)	165 (4)
O29—H29*B*···O7^{iv}	0.83 (4)	2.23 (4)	2.959 (6)	148 (5)
C13—H13···O7^{vii}	0.95	2.24	3.166 (6)	165
C17—H17···O22^{vi}	0.95	2.43	3.354 (4)	166
C18—H18···O28^{viii}	0.95	2.40	3.345 (5)	176

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