

Tetraaqua(ethane-1,2-diamine- κ^2N,N')nickel(II) naphthalene-1,5-disulfonate dihydrate

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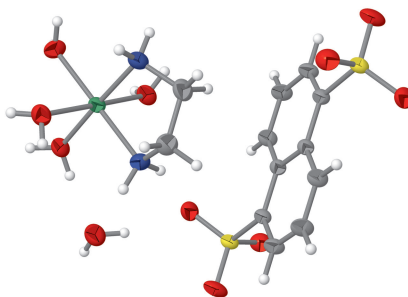
Structural data: full structural data are available from iucrdata.iucr.org

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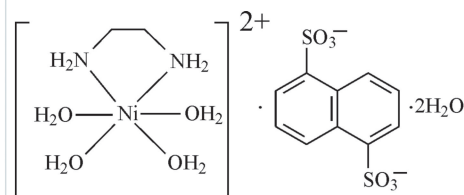
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The reaction of ethane-1,2-diamine (en, C₂H₈N₂), the sodium salt of naphthalene-1,5-disulfonic acid (H₂NDS, C₁₀H₈O₆S₂), and nickel sulfate in an aqueous solution resulted in the formation of the title salt, [Ni(C₂H₈N₂)(H₂O)₄](C₁₀H₆O₆S₂)·2H₂O or [Ni(en)(H₂O)₄](NDS)·2H₂O. In the asymmetric unit, one half of an [Ni(en)(H₂O)₄]²⁺ cation and one half of an NDS²⁻ anion, and one water molecule of crystallization are present. The Ni²⁺ cation in the complex is positioned on a twofold rotation axis and exhibits a slight tetragonal distortion of the *cis*-NiO₄N₂ octahedron, with an Ni—N bond length of 2.0782 (16) Å, and Ni—O bond lengths of 2.1170 (13) Å and 2.0648 (14) Å. The anion is completed by inversion symmetry. In the extended structure, the cations, anions, and non-coordinating water molecules are connected by intermolecular N—H...O and O—H...O hydrogen bonding, as well as C—H... π interactions, forming a three-dimensional network.

3D view



Chemical scheme



Structure description

As known for decades, ethane-1,2-diamine (en) exhibits excellent coordination and chelating abilities, forming five-membered rings with the central metals. Generally, these metallacycles adopt a twist conformation. En ligands can coordinate with metal ions in a monodentate fashion (Xue *et al.*, 2016; Mitzinger *et al.*, 2016) and in some complexes, they can act as bridging ligands (Binnemans *et al.*, 2013; Bratsos *et al.*, 2011; Doring & Jones, 2013). In most cases, en demonstrates chelating properties (Ashurov *et al.*, 2018; Qadir *et al.*, 2020). There are also metal complexes where non-coordinating en molecules are present (Sun *et al.*, 2017; Tian *et al.*, 2017; Mirzaei *et al.*, 2014).

Complexes derived from naphthalene-1,5-disulfonic acid (H₂NDS) are of great interest in supramolecular chemistry due to their ability to form hydrogen bonds (Shi *et al.*, 2014; Xu *et al.*, 2019; Chen *et al.*, 2020; Suyunov *et al.*, 2023), because the sulfonate group can accept up to six hydrogen bonds with its lone pairs (Oh *et al.*, 2020; Chen *et al.*, 2022). As a ligand, NDS²⁻ sometimes binds in a bridging mode (Lian & Qu, 2013; Das *et al.*, 2015; Tai *et al.*, 2015). As part of our work in this area, we now describe the synthesis and structure of the hydrated title salt [Ni(en)(H₂O)₄]⁺·NDS²⁻·2H₂O.

The asymmetric unit consists of one-half of the [Ni(en)(H₂O)₄]²⁺ complex cation, one half of the NDS²⁻ organic dianion, and a water molecule of crystallization. The Ni²⁺ cation in the complex is positioned on a twofold rotation axis and exhibits a slightly tetragonal distortion of the *cis*-NiO₄N₂ octahedron. The Ni–N bond length is 2.0782 (16) Å, and the Ni–O bond lengths are 2.1170 (13) Å and 2.0648 (14) Å, similar to those reported for other [Ni(en)(H₂O)₄]²⁺ complexes (Healy *et al.*, 1984). The en ligand conformation conforms to the crystallographic twofold axis that passes through it. The NDS²⁻ dianion exhibits inversion symmetry, with the inversion center located at the middle point of the C5–C5($\frac{3}{2} - x, \frac{3}{2} - y, \frac{3}{2} - z$) bond. The structures of the molecular entities are shown in Fig. 1. Neighboring anions have two distinct orientations relative to the complex cation, with the angle between their planes being 55.06 (7)°. The naphthalene ring system exhibits typical bond lengths and angles, with C–C bond lengths ranging from 1.368 (2)

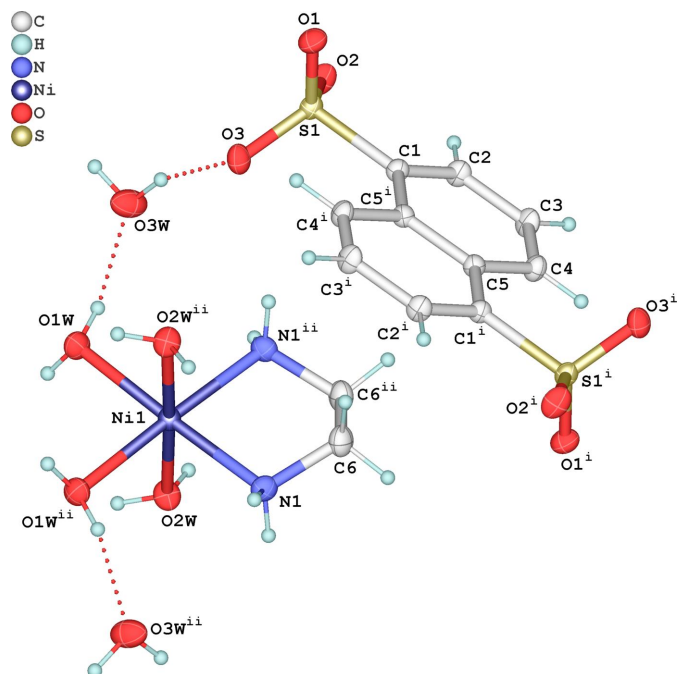


Figure 1
The structures of the molecular entities in the title salt, showing the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius and hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $\frac{3}{2} - x, \frac{3}{2} - y, \frac{3}{2} - z$; (ii) $\frac{3}{2} - x, y, 1 - z$.]

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

Cg1 and Cg2 are the centroids of the C1–C5/C5' and C1'–C5'/C5 rings, respectively, where primed atoms are related by the symmetry operation $\frac{3}{2} - x, \frac{3}{2} - y, \frac{3}{2} - z$.

| D–H···A | D–H | H···A | D···A | D–H···A |
|-----------------------------|----------|----------|-------------|---------|
| O1W–H1WA···O1 ⁱ | 0.85 (1) | 1.99 (1) | 2.8329 (19) | 171 (3) |
| O1W–H1WB···O3W | 0.85 (1) | 1.85 (1) | 2.692 (2) | 176 (3) |
| O2W–H2WA···O3 ⁱ | 0.84 (1) | 2.06 (1) | 2.8670 (19) | 160 (3) |
| O2W–H2WB···O2 ⁱⁱ | 0.85 (1) | 1.99 (1) | 2.830 (2) | 168 (3) |
| N1–H1A···O3 ⁱⁱⁱ | 0.88 (1) | 2.44 (1) | 3.274 (2) | 159 (2) |
| N1–H1B···O2 ^{iv} | 0.89 (1) | 2.36 (2) | 3.079 (2) | 139 (2) |
| O3W–H3WA···O3 | 0.85 (1) | 1.97 (1) | 2.794 (2) | 164 (3) |
| O3W–H3WB···O1 ^v | 0.84 (1) | 2.11 (1) | 2.950 (2) | 175 (3) |
| C6–H6A···Cg1 ⁱⁱⁱ | 0.97 | 2.93 | 3.755 (2) | 143 |
| C6–H6A···Cg2 ^{vi} | 0.97 | 2.93 | 3.755 (2) | 143 |
| C6–H6B···Cg1 ^{vii} | 0.97 | 2.88 | 3.781 (2) | 155 |
| C6–H6B···Cg2 | 0.97 | 2.88 | 3.781 (2) | 155 |

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

1.429 (2) Å, and C–C–C angles within the range 117.98 (18) to 123.08 (15)°.

In the crystal, the [Ni(en)(H₂O)₄]²⁺ cation, the NDS²⁻ anion, and the water molecules are associated *via* classical O–H···O and N–H···O hydrogen bonds (Table 1). Each [Ni(en)(H₂O)₄]²⁺ cation forms four N–H···O and eight O–H···O hydrogen bonds with six neighboring organic anions and two water molecules of crystallization. The four aqua and the en ligands in the cation participate exclusively as hydrogen-bonding donor groups (Fig. 2). All six acceptor O atoms of the SO₃⁻ groups of the NDS²⁻ anions participate as double acceptor atoms. It should be noted that the water molecule of crystallization (O3W) is involved in three hydrogen-bonding interactions: two as a donor group with two sulfonate O atoms from two different NDS²⁻ anions as acceptor atoms, and one as an acceptor group for a hydrogen bond with an aqua ligand. Next to Coulombic interactions, these intermolecular interactions connect the molecular building units into the three-dimensional supramolecular

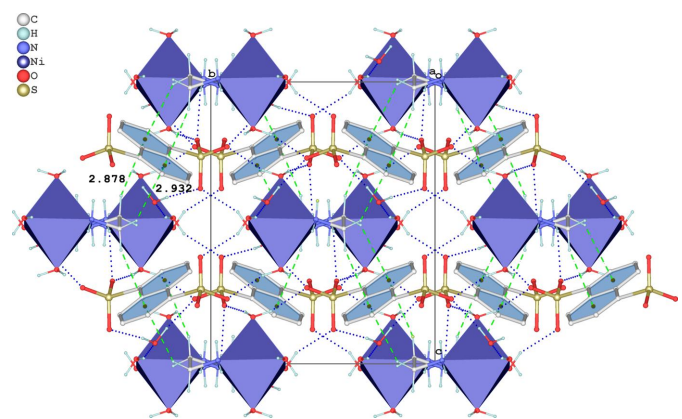


Figure 2
The crystal packing of the title salt in a view along [100]. O–H···O and N–H···O hydrogen bonds are shown as dashed blue lines, and C–H···π interactions as dashed green lines. The coordination polyhedron around Ni^{II} is given in the polyhedral representation.

structure, as depicted in Fig. 2. As a result of the steric hindrance caused by the sulfonate group, the nearest centroid distance between the naphthalene rings is 6.773 (2) Å. There are four notable C—H... π interactions between the methylene groups of the en ligands and the naphthalene rings of the NDS²⁻ anions (Table 1, Fig. 2).

Synthesis and crystallization

The commercially available starting materials were used without further purification. Ethane-1,2-diamine (0.06 g, 1.00 mmol) was added slowly to an aqueous solution of NiSO₄·7H₂O (0.28 g, 1.00 mmol), and disodium naphthalene-1,5-disulfonate (0.33 g, 1.00 mmol) was added to the resulting clear deep-blue solution. The resulting solution was set out in an open beaker at room temperature. After 7 d, block-like green crystals were obtained in 60% yield (based on Ni). Elemental analysis calculated (%) for C₁₂H₂₆N₂NiO₁₂S₂: C, 28.09; H, 5.11; N, 5.46; S, 12.50, found: C, 28.01; H, 5.06; N, 5.37; S, 12.43.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms attached to nitrogen and those of the water molecules were located in a difference-Fourier map and refined with bond-length restraints of 0.89 (1) and 0.85 (1) Å, respectively.

Acknowledgements

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Table 2

Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | [Ni(C ₂ H ₈ N ₂)(H ₂ O) ₄]- (C ₁₀ H ₆ O ₆ S ₂)·2H ₂ O |
| <i>M_r</i> | 513.18 |
| Crystal system, space group | Monoclinic, <i>I</i> 2/a |
| Temperature (K) | 291 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 15.4103 (3), 10.1338 (2), 13.4284 (2) |
| β (°) | 108.692 (2) |
| <i>V</i> (Å ³) | 1986.44 (7) |
| <i>Z</i> | 4 |
| Radiation type | Cu <i>K</i> α |
| μ (mm ⁻¹) | 3.99 |
| Crystal size (mm) | 0.28 × 0.24 × 0.2 |
| Data collection | |
| Diffractometer | XtaLAB Synergy, Single source at home/near, HyPix3000 |
| Absorption correction | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2022) |
| <i>T_{min}</i> , <i>T_{max}</i> | 0.419, 1.000 |
| No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections | 10963, 1926, 1881 |
| <i>R_{int}</i> | 0.037 |
| (<i>sin</i> θ / λ) _{max} (Å ⁻¹) | 0.615 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.030, 0.085, 1.05 |
| No. of reflections | 1926 |
| No. of parameters | 165 |
| No. of restraints | 8 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³) | 0.40, -0.33 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *OLEX2* (Dolomanov *et al.*, 2009), and *pubCIF* (Westrip, 2010).

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full crystallographic data

IUCrData (2023). **8**, x231032 [<https://doi.org/10.1107/S2414314623010325>]

Tetraaqua(ethane-1,2-diamine- κ^2N,N')nickel(II) naphthalene-1,5-disulfonate dihydrate

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Tetraaqua(ethane-1,2-diamine- κ^2N,N')nickel(II) naphthalene-1,5-disulfonate dihydrate

Crystal data

$[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{C}_{10}\text{H}_6\text{O}_6\text{S}_2) \cdot 2\text{H}_2\text{O}$

$M_r = 513.18$

Monoclinic, $I2/a$

$a = 15.4103$ (3) Å

$b = 10.1338$ (2) Å

$c = 13.4284$ (2) Å

$\beta = 108.692$ (2)°

$V = 1986.44$ (7) Å³

$Z = 4$

$F(000) = 1072$

$D_x = 1.716$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 8478 reflections

$\theta = 3.8\text{--}71.3^\circ$

$\mu = 3.99$ mm⁻¹

$T = 291$ K

Block, light green

$0.28 \times 0.24 \times 0.2$ mm

Data collection

XtaLAB Synergy, Single source at home/near,
HyPix3000

diffractometer

Radiation source: micro-focus sealed X-ray
tube, PhotonJet (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2022)

$T_{\min} = 0.419$, $T_{\max} = 1.000$

10963 measured reflections

1926 independent reflections

1881 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 71.5^\circ$, $\theta_{\min} = 3.8^\circ$

$h = -18 \rightarrow 18$

$k = -11 \rightarrow 12$

$l = -15 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.085$

$S = 1.05$

1926 reflections

165 parameters

8 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 1.9301P]$

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

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

$\Delta\rho_{\max} = 0.40$ e Å⁻³

$\Delta\rho_{\min} = -0.33$ e Å⁻³

Extinction correction: SHELXL (Sheldrick,
2015b), $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00087 (12)

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|--------------|----------------------------------|
| Ni1 | 0.750000 | 0.31595 (4) | 0.500000 | 0.02364 (16) |
| O1W | 0.66391 (10) | 0.16745 (13) | 0.51659 (11) | 0.0345 (3) |
| H1WA | 0.6474 (19) | 0.106 (2) | 0.4714 (17) | 0.055 (8)* |
| H1WB | 0.6172 (15) | 0.191 (3) | 0.532 (3) | 0.069 (10)* |
| O2W | 0.69189 (10) | 0.31220 (13) | 0.33422 (11) | 0.0341 (3) |
| H2WA | 0.6830 (19) | 0.2367 (15) | 0.306 (2) | 0.051 (7)* |
| H2WB | 0.6401 (11) | 0.350 (3) | 0.312 (2) | 0.059 (8)* |
| N1 | 0.83603 (11) | 0.46867 (16) | 0.48778 (13) | 0.0301 (3) |
| H1A | 0.8373 (19) | 0.473 (3) | 0.4228 (11) | 0.048 (7)* |
| H1B | 0.8942 (9) | 0.459 (2) | 0.5276 (18) | 0.050 (7)* |
| C6 | 0.80179 (13) | 0.59247 (19) | 0.52035 (16) | 0.0363 (4) |
| H6A | 0.825144 | 0.667734 | 0.492234 | 0.044* |
| H6B | 0.822909 | 0.599187 | 0.596421 | 0.044* |
| S1 | 0.57628 (3) | 0.54449 (4) | 0.76422 (3) | 0.02430 (16) |
| O1 | 0.59637 (9) | 0.54691 (13) | 0.87797 (10) | 0.0337 (3) |
| O2 | 0.47965 (9) | 0.56091 (14) | 0.70702 (11) | 0.0369 (3) |
| O3 | 0.61490 (9) | 0.42790 (12) | 0.73007 (11) | 0.0343 (3) |
| C1 | 0.63244 (11) | 0.68365 (16) | 0.73175 (13) | 0.0231 (3) |
| C2 | 0.57843 (12) | 0.78162 (18) | 0.67353 (14) | 0.0281 (4) |
| H2 | 0.514988 | 0.774290 | 0.653357 | 0.034* |
| C3 | 0.61849 (12) | 0.89311 (18) | 0.64417 (14) | 0.0301 (4) |
| H3 | 0.581294 | 0.959325 | 0.604714 | 0.036* |
| C4 | 0.71119 (12) | 0.90538 (17) | 0.67283 (14) | 0.0274 (4) |
| H4 | 0.736531 | 0.979213 | 0.651599 | 0.033* |
| C5 | 0.76989 (12) | 0.80698 (15) | 0.73475 (13) | 0.0224 (3) |
| O3W | 0.52056 (11) | 0.25077 (18) | 0.57325 (13) | 0.0495 (4) |
| H3WA | 0.540 (2) | 0.304 (2) | 0.6243 (16) | 0.062 (9)* |
| H3WB | 0.485 (2) | 0.196 (3) | 0.588 (3) | 0.076 (11)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|------------|-------------|---------------|--------------|--------------|
| Ni1 | 0.0186 (2) | 0.0240 (2) | 0.0265 (2) | 0.000 | 0.00471 (17) | 0.000 |
| O1W | 0.0315 (7) | 0.0306 (7) | 0.0426 (8) | −0.0085 (5) | 0.0135 (6) | −0.0048 (6) |
| O2W | 0.0309 (7) | 0.0348 (7) | 0.0307 (7) | 0.0010 (6) | 0.0017 (6) | −0.0023 (5) |
| N1 | 0.0231 (7) | 0.0330 (8) | 0.0338 (8) | −0.0030 (6) | 0.0086 (6) | 0.0004 (6) |
| C6 | 0.0348 (11) | 0.0275 (9) | 0.0436 (10) | −0.0046 (8) | 0.0085 (8) | −0.0027 (8) |
| S1 | 0.0179 (2) | 0.0253 (2) | 0.0283 (2) | −0.00158 (14) | 0.00546 (17) | 0.00269 (14) |
| O1 | 0.0335 (7) | 0.0381 (7) | 0.0309 (7) | 0.0009 (5) | 0.0123 (6) | 0.0064 (5) |

| | | | | | | |
|-----|------------|-------------|------------|-------------|------------|-------------|
| O2 | 0.0184 (7) | 0.0412 (7) | 0.0459 (8) | -0.0040 (5) | 0.0030 (6) | 0.0088 (6) |
| O3 | 0.0322 (7) | 0.0258 (6) | 0.0431 (7) | -0.0022 (5) | 0.0097 (6) | -0.0036 (5) |
| C1 | 0.0185 (8) | 0.0247 (8) | 0.0249 (8) | -0.0009 (6) | 0.0053 (6) | 0.0003 (6) |
| C2 | 0.0181 (8) | 0.0308 (9) | 0.0324 (9) | 0.0023 (7) | 0.0039 (7) | 0.0040 (7) |
| C3 | 0.0220 (8) | 0.0281 (9) | 0.0360 (9) | 0.0067 (7) | 0.0034 (7) | 0.0099 (7) |
| C4 | 0.0235 (8) | 0.0243 (8) | 0.0325 (8) | 0.0008 (6) | 0.0064 (7) | 0.0060 (7) |
| C5 | 0.0197 (8) | 0.0232 (8) | 0.0230 (8) | 0.0004 (6) | 0.0049 (6) | -0.0002 (6) |
| O3W | 0.0438 (9) | 0.0612 (10) | 0.0485 (9) | -0.0163 (8) | 0.0219 (7) | -0.0165 (8) |

Geometric parameters (Å, °)

| | | | |
|--|-------------|-------------------------|-------------|
| Ni1—O1W ⁱ | 2.0648 (14) | S1—O1 | 1.4583 (14) |
| Ni1—O1W | 2.0648 (14) | S1—O2 | 1.4498 (13) |
| Ni1—O2W | 2.1170 (13) | S1—O3 | 1.4612 (14) |
| Ni1—O2W ⁱ | 2.1170 (13) | S1—C1 | 1.7803 (17) |
| Ni1—N1 | 2.0782 (16) | C1—C2 | 1.368 (2) |
| Ni1—N1 ⁱ | 2.0783 (15) | C1—C5 ⁱⁱ | 1.429 (2) |
| O1W—H1WA | 0.847 (10) | C2—H2 | 0.9300 |
| O1W—H1WB | 0.846 (10) | C2—C3 | 1.403 (3) |
| O2W—H2WA | 0.844 (10) | C3—H3 | 0.9300 |
| O2W—H2WB | 0.849 (10) | C3—C4 | 1.361 (2) |
| N1—H1A | 0.880 (10) | C4—H4 | 0.9300 |
| N1—H1B | 0.889 (10) | C4—C5 | 1.422 (2) |
| N1—C6 | 1.480 (2) | C5—C5 ⁱⁱ | 1.428 (3) |
| C6—C6 ⁱ | 1.512 (4) | O3W—H3WA | 0.846 (10) |
| C6—H6A | 0.9700 | O3W—H3WB | 0.844 (10) |
| C6—H6B | 0.9700 | | |
| O1W ⁱ —Ni1—O1W | 86.43 (8) | N1—C6—H6A | 109.9 |
| O1W ⁱ —Ni1—O2W | 86.76 (6) | N1—C6—H6B | 109.9 |
| O1W—Ni1—O2W | 91.75 (6) | C6 ⁱ —C6—H6A | 109.9 |
| O1W ⁱ —Ni1—O2W ⁱ | 91.74 (6) | C6 ⁱ —C6—H6B | 109.9 |
| O1W—Ni1—O2W ⁱ | 86.76 (6) | H6A—C6—H6B | 108.3 |
| O1W ⁱ —Ni1—N1 | 94.94 (6) | O1—S1—O3 | 111.79 (8) |
| O1W ⁱ —Ni1—N1 ⁱ | 178.02 (6) | O1—S1—C1 | 106.65 (8) |
| O1W—Ni1—N1 | 178.02 (6) | O2—S1—O1 | 112.96 (8) |
| O1W—Ni1—N1 ⁱ | 94.94 (6) | O2—S1—O3 | 112.27 (8) |
| O2W ⁱ —Ni1—O2W | 177.95 (8) | O2—S1—C1 | 106.06 (8) |
| N1—Ni1—O2W | 89.77 (6) | O3—S1—C1 | 106.55 (8) |
| N1—Ni1—O2W ⁱ | 91.76 (6) | C2—C1—S1 | 117.40 (13) |
| N1 ⁱ —Ni1—O2W ⁱ | 89.77 (6) | C2—C1—C5 ⁱⁱ | 121.20 (15) |
| N1 ⁱ —Ni1—O2W | 91.77 (6) | C5 ⁱⁱ —C1—S1 | 121.41 (12) |
| N1—Ni1—N1 ⁱ | 83.73 (9) | C1—C2—H2 | 119.9 |
| Ni1—O1W—H1WA | 120.8 (19) | C1—C2—C3 | 120.19 (16) |
| Ni1—O1W—H1WB | 117 (2) | C3—C2—H2 | 119.9 |
| H1WA—O1W—H1WB | 107 (3) | C2—C3—H3 | 119.6 |
| Ni1—O2W—H2WA | 116.0 (19) | C4—C3—C2 | 120.71 (16) |
| Ni1—O2W—H2WB | 113 (2) | C4—C3—H3 | 119.6 |

| | | | |
|---------------------------|--------------|---------------------------------------|--------------|
| H2WA—O2W—H2WB | 105 (3) | C3—C4—H4 | 119.5 |
| Ni1—N1—H1A | 109.5 (17) | C3—C4—C5 | 120.97 (16) |
| Ni1—N1—H1B | 114.7 (17) | C5—C4—H4 | 119.5 |
| H1A—N1—H1B | 105 (2) | C4—C5—C1 ⁱⁱ | 123.08 (15) |
| C6—N1—Ni1 | 108.12 (12) | C4—C5—C5 ⁱⁱ | 118.94 (19) |
| C6—N1—H1A | 112.0 (17) | C5 ⁱⁱ —C5—C1 ⁱⁱ | 117.98 (18) |
| C6—N1—H1B | 107.4 (17) | H3WA—O3W—H3WB | 108 (3) |
| N1—C6—C6 ⁱ | 109.15 (12) | | |
| | | | |
| Ni1—N1—C6—C6 ⁱ | -38.8 (2) | O3—S1—C1—C5 ⁱⁱ | -53.25 (16) |
| S1—C1—C2—C3 | -179.17 (14) | C1—C2—C3—C4 | 0.1 (3) |
| O1—S1—C1—C2 | -113.59 (15) | C2—C3—C4—C5 | -1.1 (3) |
| O1—S1—C1—C5 ⁱⁱ | 66.29 (15) | C3—C4—C5—C1 ⁱⁱ | -178.96 (17) |
| O2—S1—C1—C2 | 7.07 (16) | C3—C4—C5—C5 ⁱⁱ | 1.1 (3) |
| O2—S1—C1—C5 ⁱⁱ | -173.05 (14) | C5 ⁱⁱ —C1—C2—C3 | 1.0 (3) |
| O3—S1—C1—C2 | 126.87 (14) | | |

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

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

*Cg*1 and *Cg*2 are the centroids of the C1—C5/C5' and C1'—C5'/C5 rings, respectively, where primed atoms are related by the symmetry operation $3/2 - x, 3/2 - y, 3/2 - z$.

| <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 <i>W</i> —H1 <i>WA</i> ...O1 ⁱⁱⁱ | 0.85 (1) | 1.99 (1) | 2.8329 (19) | 171 (3) |
| O1 <i>W</i> —H1 <i>WB</i> ...O3 <i>W</i> | 0.85 (1) | 1.85 (1) | 2.692 (2) | 176 (3) |
| O2 <i>W</i> —H2 <i>WA</i> ...O3 ⁱⁱⁱ | 0.84 (1) | 2.06 (1) | 2.8670 (19) | 160 (3) |
| O2 <i>W</i> —H2 <i>WB</i> ...O2 ^{iv} | 0.85 (1) | 1.99 (1) | 2.830 (2) | 168 (3) |
| N1—H1 <i>A</i> ...O3 ⁱ | 0.88 (1) | 2.44 (1) | 3.274 (2) | 159 (2) |
| N1—H1 <i>B</i> ...O2 ^v | 0.89 (1) | 2.36 (2) | 3.079 (2) | 139 (2) |
| O3 <i>W</i> —H3 <i>WA</i> ...O3 | 0.85 (1) | 1.97 (1) | 2.794 (2) | 164 (3) |
| O3 <i>W</i> —H3 <i>WB</i> ...O1 ^{vi} | 0.84 (1) | 2.11 (1) | 2.950 (2) | 175 (3) |
| C6—H6 <i>A</i> ... <i>Cg</i> 1 ⁱ | 0.97 | 2.93 | 3.755 (2) | 143 |
| C6—H6 <i>A</i> ... <i>Cg</i> 2 ^{vii} | 0.97 | 2.93 | 3.755 (2) | 143 |
| C6—H6 <i>B</i> ... <i>Cg</i> 1 ⁱⁱ | 0.97 | 2.88 | 3.781 (2) | 155 |
| C6—H6 <i>B</i> ... <i>Cg</i> 2 | 0.97 | 2.88 | 3.781 (2) | 155 |

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