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

Hai Le Thi Hong, Vinh Nguyen Thi Ngoc, Da Tran Thi, Ngan Nguyen Bich and Luc Van Meervelt

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Hai Le Thi Hong,* Vinh Nguyen Thi Ngoc,* Da Tran Thi,* Ngan Nguyen Bicha and Luc Van Meerveltb

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The asymmetric unit of the title compound, [Ni(H$_2$O)$_6$][(C$_{11}$H$_8$NO$_8$S)$_2$]·2H$_2$O, 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, plasmooquine and acrifluine, for instance, are known to be able to cure malaria (Foley & Tilley, 1998; Długosz & Dusz, 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.
by IR or \(^1\)H NMR spectroscopic methods. The spectroscopic data are different from those obtained for free \(\text{QOH}\) and in favour of a deprotonated carboxylic acid group, but give no indication about a possible complex formation. X-ray diffraction now shows that \(\text{QOH}\) is not complexing directly with \(\text{Ni}^{\text{II}}\).

2. Structural commentary

The structure determination shows that the carboxyl group of \(\text{QOH}\) is deprotonated and the anion is present in its zwitter-ionic form (Fig. 1), which was also observed for \(\text{Q}\) (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)\(^\circ\) 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). \(\text{QOH}\), however, is not acting as a ligand for \(\text{Ni}^{\text{II}}\), which occurs as a hexaaqua complex. This [\(\text{Ni(H}_2\text{O)}_6\)]\(^{2+}\) is located about an inversion center and has an octahedral

![Figure 1](image1)

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

![Figure 2](image2)

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

![Figure 3](image3)

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

### Table 1

<table>
<thead>
<tr>
<th>Hydrogen-bond geometry (Å, °)</th>
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<tr>
<td>(D-H\cdots A)</td>
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<tr>
<td>O2—H2A···O27(^a)</td>
</tr>
<tr>
<td>O2—H2B···O29(^{ii})</td>
</tr>
<tr>
<td>O3—H3A···O8(^{iv})</td>
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<tr>
<td>O3—H3B···O6(^{vi})</td>
</tr>
<tr>
<td>O4—H4A···O28(^{v})</td>
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<tr>
<td>O4—H4B···O6</td>
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<tr>
<td>O5—H5A···O4(^{vii})</td>
</tr>
<tr>
<td>O22—H22···O8(^{vi})</td>
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<tr>
<td>O23—H23···O29(^{viii})</td>
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<tr>
<td>O29—H29A···O27(^{ix})</td>
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<tr>
<td>O29—H29B···O7(^{x})</td>
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<tr>
<td>C13—H13···O7(^{xii})</td>
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<tr>
<td>C17—H17···O22(^{xii})</td>
</tr>
<tr>
<td>C18—H18···O28(^{xii})</td>
</tr>
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</table>

Symmetry codes: (i) \(-x+2, -y+2, -z+1\); (ii) \(-x+2, -y+2, -z+1\); (iii) \(x+1, y, z\); (iv) \(-x+2, -y+2, -z+1\); (v) \(x, y+1, z\); (vi) \(-x+1, -y+1, -z+1\); (vii) \(-x+1, -y+2, -z+2\); (viii) \(-x+2, -y+3, -z+1\).
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 hexaaxa 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 NiCl2·6H2O (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 1:1 v/v solution at room temperature. IR (Impack-410 Nicolet spec-rometer, KBr, cm−1): 3420 (vOH); 3080, 2918 (vCH); 1620 (vC=O); 1426 (vC=O); 1528 (vC=C or vC=N); 466 (vN=O). 1H NMR (Bruker Avance 500 MHz, d6-DMSO): δ 8.74 (1H, s, Ar), 8.17 (1H, s, Ar), 7.2 (1H, s, Ar), 4.64 (2H, s, CH2); (Bruker Avance 500 MHz, D2O): δ 9.26 (1H, s, Ar), 7.01 (1H, s, Ar), 4.80 (2H, s, CH2).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms H2B, H3B, H4B, H14, H29A and H29B 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, Uiso(H) values were assigned as 1.2Ueq of the parent atoms (1.5Ueq for H22 and H23). The SO3 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.

Acknowledgements

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References


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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

\[\text{[Ni(H}_2\text{O})_6]\text{(C}_{11}\text{H}_8\text{NO}_8\text{S})_2\cdot2\text{H}_2\text{O}\]

\(M_r = 831.31\)

Triclinic, \(\overline{P}\)

\(a = 8.1632 (5)\) Å

\(b = 8.2829 (6)\) Å

\(c = 11.8492 (8)\) Å

\(\alpha = 102.316 (6)^\circ\)

\(\beta = 102.250 (6)^\circ\)

\(\gamma = 93.003 (6)^\circ\)

\(V = 760.91 (9)\) 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

\(\theta = 3.4–28.9^\circ\)

\(\mu = 0.88\) 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\(^{-1}\)

\(\omega\) scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2012)

\(T_{\text{min}} = 0.781, T_{\text{max}} = 1.000\)

8135 measured reflections

3071 independent reflections

2513 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.025\)

\(\theta_{\text{max}} = 26.4^\circ, \theta_{\text{min}} = 2.8^\circ\)

\(h = -10\rightarrow10\)

\(k = -10\rightarrow10\)

\(l = -14\rightarrow14\)

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
\[ w = \frac{1}{\sigma^2(F_{o}^2) + (0.0452P)^2 + 1.8778P} \]

where \( P = (F_{o}^2 + 2F_{c}^2)/3 \)

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

### 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)**

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<th>z</th>
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**Atomic displacement parameters (Å²)**

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<th>U¹³</th>
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**Geometric parameters (Å, °)**

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| Ni1—O2i | 2.038 (2) | C15—C16 | 1.423 (5) |
| Ni1—O3i | 2.034 (3) | C15—C18 | 1.409 (4) |</p>
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<td>O23—C20—C21—O22</td>
<td>−0.2 (5)</td>
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<tr>
<td>N14—C15—C16—C21</td>
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<td>O24—C19—C20—C21</td>
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<td>O24—C25—C26—O28</td>
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Symmetry code: (i) −x+2, −y+1, −z+2.

**Hydrogen-bond geometry (Å, °)**

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<th>D—H···H</th>
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<th>H···A</th>
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<td>2.718 (5)</td>
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<td>O3—H3B···O6i</td>
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<td>2.05 (5)</td>
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<td>D(H) (A)</td>
<td>D(O-H) (A)</td>
<td>Angle (°)</td>
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<tr>
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<td>C17—H17···O22vii</td>
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<td>3.345 (5)</td>
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Symmetry codes: (i) −x+2, −y+1, −z+2; (ii) −x+2, −y+2, −z+2; (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.