

Tetraqua(8-hydroxyquinoline-5-sulfonato-*N,O*)-nickel(II) monohydrate

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Key indicators

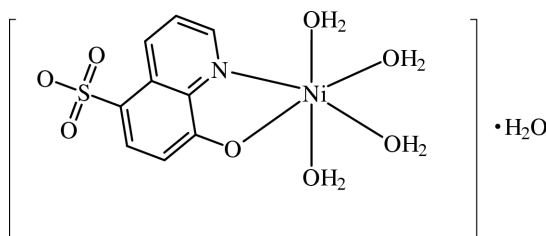
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.023
wR factor = 0.062
Data-to-parameter ratio = 12.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $[\text{Ni}(\text{HQS})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (HQS is the 8-hydroxyquinoline-5-sulfonic acid dianion, $\text{C}_9\text{H}_{13}\text{NO}_8\text{S}$), the Ni^{II} ion is coordinated by the N and quinolinolate-O atoms of HQS and four water molecules, exhibiting a distorted octahedral geometry. The sulfonic O atoms of HQS are not involved in the coordination. However, the sulfonic O atoms along with the coordinated and lattice water molecules play a vital role in assembling the three-dimensional structure by an extensive network of intermolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. Furthermore, the overall structure is stabilized by $\pi-\pi$ stacking interactions between the ring moieties of HQS in the neighbouring complex molecules.

Comment

Oxine (8-hydroxyquinoline) and its derivatives are well known analytical reagents for metal ions and form well defined chelate complexes with many transition metals (Hollingsheard, 1956). Some of these compounds also act as potential antibacterial and anti-amoebic agents. Metal chelation has been implicated in their biological activity (Martel & Calvin, 1959). The incorporation of sulfonic acid in the oxine moiety provides additional metal binding sites as well as hydrogen-bonding acceptor sites. This type of ligand is called sulfoxine.



(I)

In metal-oxinate systems, the chelation of the metal is achieved through N atoms and deprotonated quinolinol-O atoms. However, in metal sulfoxinates, in addition to the normal metal chelation by the oxine moiety, one of the sulfonic O atoms is also coordinated to the metal. This sulfonic O-atom binding can occur in two different coordination modes. In one mode, two inversion-related monomers are bridged by one of the sulfonic acid-O atoms involved in coordination, leading to a cage-like dimer. This has been observed in the copper sulfoxinate complexes (Petit, Coquerel *et al.*, 1993; Petit, Ammor *et al.*, 1993) and a cobalt complex of 7-iodo-8-hydroxyquinoline-5-sulfonic acid (ferron; Muthiah *et al.*, 2001). In another mode, a sulfonic acid-O atom of one

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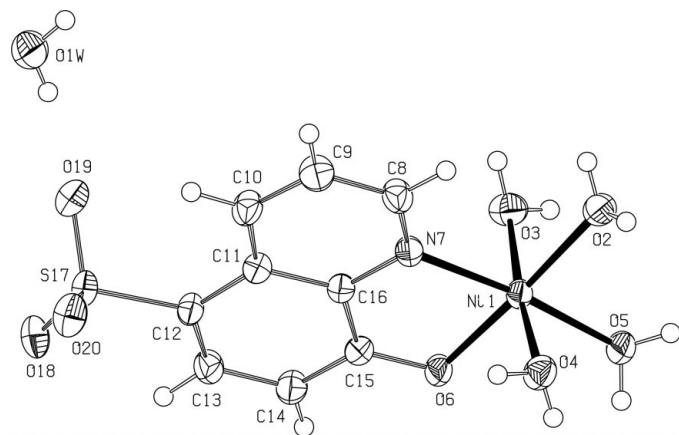


Figure 1

A view of (I) with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

molecule is coordinated to the metal of another molecule leading to a one-dimensional polymeric arrangement (Petit, Coquerel *et al.*, 1993). The various remarkable structural features observed in different metal complexes of HQS have prompted us to investigate the crystal structure of the title nickel^{II} complex, (I).

In (I), the geometry around the nickel ion is a distorted octahedron (Fig. 1). The N and O atoms of the quinolinol moiety and the two water molecules (O2 and O5) are coordinated to the metal in the equatorial positions. Another two water molecules (O3 and O4) occupy the axial positions in order to complete the octahedron. The axial Ni–O(water) distances are slightly longer than the equatorial distances. The Ni–O(quinolinol) bond is shorter than the Ni–N bond by 0.045 Å, as expected (Palenik, 1964). The basic assumption is that the electronegativities of oxygen and nitrogen are not changed relative to one another.

The sulfonic acid group is not involved in metal coordination but makes an extensive network of hydrogen bonds with all the coordinated water molecules and a free water molecule, O1 (Table 2). Hydrogen-bonding patterns involving the sulfonate anion in biological systems and metal complexes are of current interest (Onoda *et al.*, 2001). The coordinated water molecules O2 and O3 make hydrogen bonds with atoms O19 and O18, respectively, of a symmetry-related ($\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$) sulfonic acid group. The O atom of the same symmetry-related quinolinol moiety and one of the sulfonic acid-O atoms, O19, are bridged by the free water molecule. These intermolecular hydrogen-bonding interactions involving the sulfonic acid group and the water molecules form a head-to-tail hydrogen-bonded dimer-like arrangement (Fig. 2). On the other hand, the complex units are connected through coordinated water molecules O2 and O4 by a pair of symmetry-related ($-x, 1-y, 1-z$) O2–H \cdots O4 hydrogen bonds, as shown in Fig. 3. All these hydrogen-bonding interactions, together with the remaining O–H \cdots O hydrogen bonds between water mol-

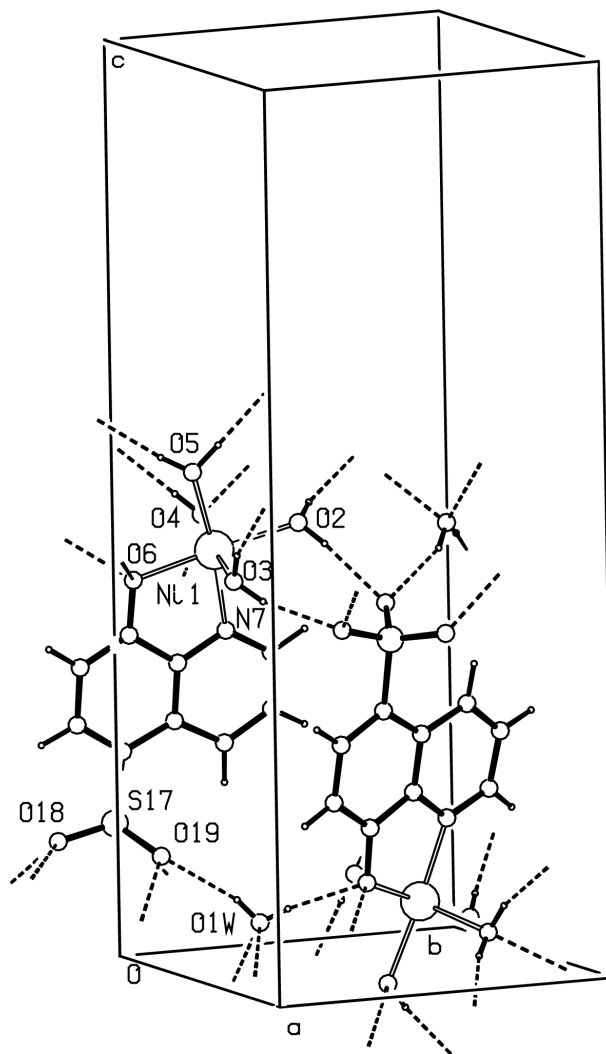
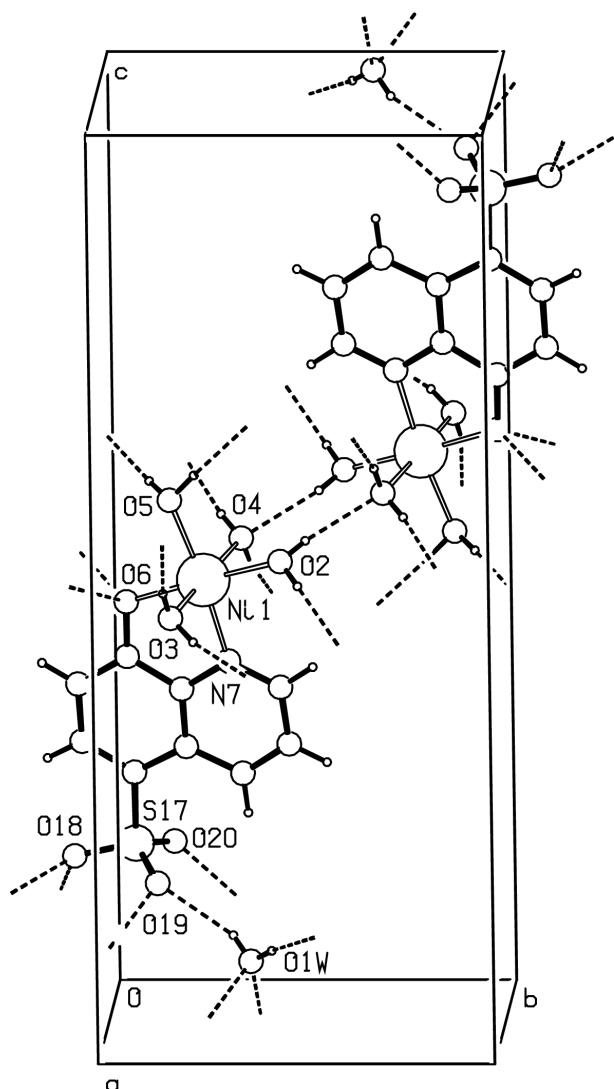


Figure 2

A view of the head-to-tail hydrogen-bonded dimer-like arrangement.

ecules and the sulfonic acid group, assemble the molecules into a supramolecular three-dimensional network, as depicted in Fig. 4. As can be seen in Fig. 4, each complex unit is stacked along the *a* axis between two neighbouring symmetry-related units, *viz.* ($1/2-x, 1/2+y, 1/2-z$) and ($1/2-x, 1/2+y, 1/2-z$). The average value of the dihedral angles between the pyridine and phenyl rings in the neighbouring HQS ligands is 18.9 (5)°. The minimum slip angles [34.1 (4)° and 24.8 (1)°, angle between the centroid vector and the normal to the planes] are observed between the corresponding pyridine and phenyl rings in adjacent complex units, which shows that the pyridine–phenyl stacking alignment is better compared to pyridine–pyridine or phenyl–phenyl stacking. The interplanar and centroid-to-centroid distances between corresponding pyridine and phenyl rings in adjacent complex units are 3.276 (4) and 3.949 (7) Å, and 4.350 (15) and 4.707 (5) Å, respectively. The sulfonic acid-O atoms are also involved in weak C–H \cdots O hydrogen-bonding interactions. This type of weak C–

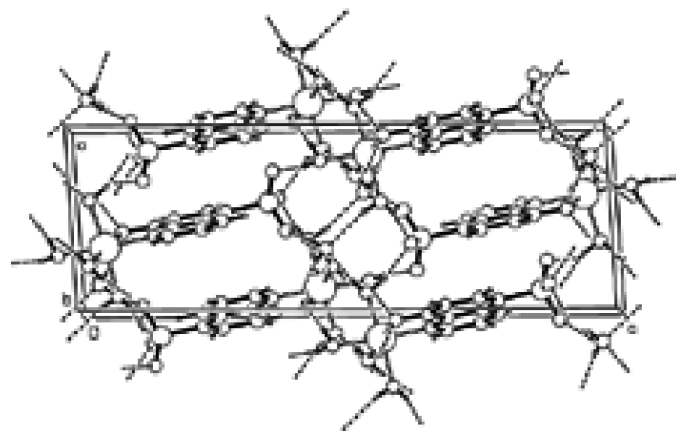

Figure 3

A view of the O—H...O bonds connecting two HQS ligands coordinated to Ni^{II}.

H...O hydrogen bonding has also been observed in the crystal structures of 8-hydroxyquinoline-7-iodo-5-sulfonic acid (Balasubramanian & Muthiah, 1996a), 8-hydroxyquinoline-7-nitro-5-sulfonic acid (Balasubramanian & Muthiah, 1996b) and cobalt-sulfoxinate (Muthiah *et al.*, 2001).

Experimental

To a suspension of NiCO₃·2[Ni(OH)₂]-4H₂O (1 mmol, 0.0627 g) in 50 ml of water, drops of dilute HCl (1 N, 5 ml) were added to obtain a clear solution. 8-Hydroxyquinoline-5-sulfonic acid monohydrate (MERCK-Schuchardt; 1 mmol, 0.122 g) was dissolved in 40 ml of water. The above solutions were mixed and stirred and warmed for about an hour. Crystals of (I) were obtained from an aqueous solution.


Figure 4

The supramolecular three-dimensional network structure of (I).

Crystal data

[Ni(C₉H₁₃NO₈S)]·H₂O
M_r = 371.99
 Monoclinic, *P*2₁/*n*
a = 7.366 (2) Å
b = 9.000 (2) Å
c = 21.456 (2) Å
 β = 93.73 (2)°
V = 1419.4 (5) Å³
Z = 4

D_x = 1.741 Mg m⁻³
 MoK α radiation
 Cell parameters from 25 reflections
 θ = 1.9–28.0°
 μ = 1.56 mm⁻¹
T = 293 (2) K
 Prism, green
 0.36 × 0.29 × 0.25 mm

Data collection

Bruker AXS SMART diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.519, *T_{max}* = 0.678
 14764 measured reflections
 3222 independent reflections
 2925 reflections with *I* > 2 σ (*I*)

R_{int} = 0.023
 θ_{\max} = 28.1°
h = -9 → 9
k = -11 → 11
l = -28 → 28
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.023
wR(*F*²) = 0.062
S = 1.02
 3222 reflections
 251 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.4020P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.009$
 $\Delta\rho_{\max} = 0.13 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.10 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1—O2	2.0601 (14)	Ni1—O5	2.0585 (12)
Ni1—O3	2.0945 (14)	Ni1—O6	2.0209 (12)
Ni1—O4	2.0852 (13)	Ni1—N7	2.0658 (14)
O2—Ni1—O3	88.00 (6)	O3—Ni1—N7	91.94 (6)
O2—Ni1—O4	87.28 (6)	O4—Ni1—O5	89.44 (5)
O2—Ni1—O5	89.28 (5)	O4—Ni1—O6	96.69 (5)
O2—Ni1—O6	175.96 (5)	O4—Ni1—N7	90.24 (5)
O2—Ni1—N7	97.35 (5)	O5—Ni1—O6	91.50 (5)
O3—Ni1—O4	175.02 (6)	O5—Ni1—N7	173.34 (5)
O3—Ni1—O5	88.91 (6)	O6—Ni1—N7	81.93 (5)
O3—Ni1—O6	88.05 (5)		

Table 2
Hydrogen-bonding 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—H1···O19	0.74 (3)	2.12 (3)	2.824 (2)	159 (3)
O1—H1'···O6 ⁱ	0.73 (3)	2.12 (3)	2.830 (2)	165 (3)
O2—H2···O19 ^j	0.81 (2)	1.96 (3)	2.7644 (19)	170 (2)
O2—H2'···O4 ⁱⁱ	0.79 (3)	2.11 (3)	2.879 (2)	166 (3)
O3—H3···O18 ^k	0.82 (3)	1.98 (3)	2.7756 (19)	165 (3)
O3—H3'···O1 ⁱⁱⁱ	0.76 (3)	2.16 (3)	2.900 (2)	162 (3)
O4—H4···O1 ^{iv}	0.78 (3)	1.93 (3)	2.690 (2)	166 (3)
O4—H4'···O18 ^v	0.82 (3)	1.93 (2)	2.7133 (18)	161 (2)
O5—H5···O6 ^{vi}	0.83 (2)	1.94 (2)	2.7677 (18)	172 (2)
O5—H5'···O20 ⁱⁱⁱ	0.87 (3)	1.94 (3)	2.8075 (18)	169 (2)
C8—H8···O19 ^j	0.964 (18)	2.534 (16)	3.267 (2)	132.8 (12)
C13—H13···O18	0.970 (18)	2.399 (19)	2.831 (2)	106.4 (13)
C14—H14···O20 ^{vii}	0.937 (19)	2.48 (2)	3.262 (2)	141.2 (18)

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

H atoms were all localized in difference Fourier maps, and were refined with isotropic displacement parameters. The C—H and O—H bond lengths are in the ranges 0.941 (2)–0.973 (3) and 0.735 (4)–0.876 (5) Å, respectively.

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure:

SHELXL97 (Sheldrick, 1997); molecular graphics: *PLATON97* (Spek, 1997); software used to prepare material for publication: *PLATON97*.

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