metal-organic papers

The interplay of coordination, π–π stacking and hydrogen bonding in the supramolecular self-assembly of bis(μ-7-iodo-8-hydroxyquinoline-5-sulfonato-$\kappa^3 N,O:O'$)bis[triaquanickel(II)] tetrahydrate

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The title compound, $[\text{Ni}(\text{C}_9\text{H}_4\text{INO}_6\text{S})_2(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$, is isomorphous with the corresponding cobalt(II) complex of ferron. Two inversion-related ligands and two Ni$^{\text{II}}$ atoms form a cage-like dimer. Both ligands of the dimer are bridged by a pair of inversion-related Ni—O(sulfonate) bonds. The octahedral coordination geometry of nickel(II) is made up of the ring N atom, the deprotonated quinolinol O atom (the usual bidentate chelation), one of the sulfonate O atoms, and three water molecules. The ligands in the dimer are stacked over one another. This architecture is further stabilized by a number of O—H···O hydrogen bonds involving the deprotonated quinolinol O atom, sulfonate O atoms, and uncoordinated and coordinated water molecules.

Comment

Oxine (8-hydroxyquinoline) and its derivatives are widely used as analytical reagents and anti-amoebic agents (Bambury, 1979). Oxine, in its deprotonated form, is a bidentate chelator, forming complexes with a number of metal ions. The deprotonated O atom and the ring N atom are involved in the metal chelation. Metal chelation has been implicated in the biological activity of derivatives of oxine (Martel & Calvin, 1959). The introduction of sulfonic acid in the oxine moiety offers additional metal-binding and

(I)
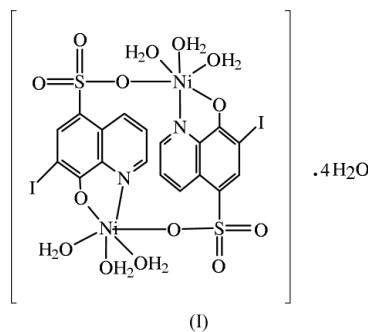
hydrogen-bonding sites/modes. This type of ligand is called sulfoxine (sulfonic acid + oxine). Hydrogen-bonding patterns and metal-binding modes of sulfoxines are of current interest (Cai, Chen, Liao, Feng & Chen, 2001; Cai, Chen, Liao, Yao *et al.*, 2001; Cai, Chen, Feng *et al.*, 2001). The crystal structures of 7-iodo-8-hydroxyquinoline-5-sulfonic acid (ferron; Balasu-bramanian & Muthiah, 1996*a*), 7-nitro-8-hydroxyquinoline-5-
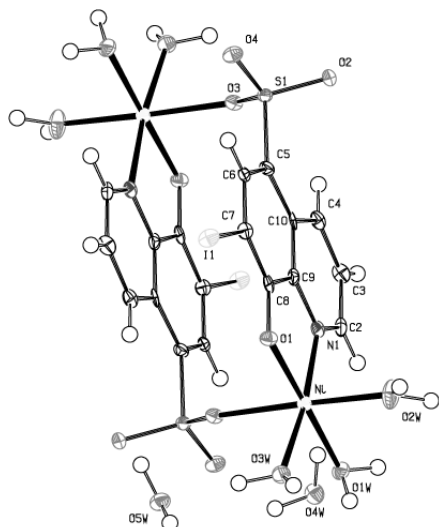
Figure 1
View of the title dimeric complex, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

sulfonic acid monohydrate (Balasubramanian & Muthiah, 1996b), a cobalt(II) complex of ferron (Balasubramanian, 1995), a nickel complex of 8-hydroxyquinoline-5-sulfonic acid (NiHQS; Baskar Raj *et al.*, 2001), a sodium complex of HQS (Baskar Raj *et al.*, 2002) and a lithium complex of HQS (Murugesan & Muthiah, 1997) have also been reported from our laboratory. To gain more insight into the metal-binding modes and hydrogen-bonding patterns of sulfoxines, the title compound, (I), has been investigated.

The present nickel complex is isomorphous with the cobalt complex(II) of ferron (Balasubramanian, 1995). Two inversion-related ligands and two Ni^{II} atoms form a cage-like dimer. Both ligands of the dimer are bridged by a pair of inversion-related Ni—O(sulfonate) bonds. The octahedral coordination geometry of nickel(II) is made up of a ring N atom, the deprotonated quinolinol O atom (the usual bidentate chelation), one of the sulfonate O atoms and three water molecules (Fig. 1). Selected bond lengths and angles, including the coordination geometry of Ni^{II}, are given in Table 1. The quinolinol O atom, N atom and two water molecules (O1W and O3W) constitute the equatorial plane, as they do also in NiHQS. One of the sulfonate O atoms (O3) and another water molecule (O2W) occupy the axial sites. The axial Ni—OW distance is slightly longer than the equatorial Ni—OW distances. This trend has also been noted in NiHQS. The Ni—O(quinolinol) and Ni—N distances observed in (I) agree with those reported for NiHQS. The Ni—O(sulfonate) distance is significantly longer than the Ni—OW distances. The bite angle (N1—Ni1—O1) in (I) is 81.84 (11)°; the corresponding parameter in NiHQS is 81.93 (5)°. This mode of binding is in contrast to that observed in one form of copper sulfoxinate (Petit *et al.*, 1993), where the ligands are arranged linearly in a head-to-tail manner, leading to a chain motif, and the ligands are bridged by a metal–oxygen (sulfonate) bond. However, in both modes of binding, the usual bidentate chelation of the

oxine moiety is maintained. Interestingly, in the crystal structure of NiHQS, only the usual bidentate chelation of the oxine motif has been observed and there is no involvement of the sulfonate group in metal binding. However, this sulfonate group is involved in extensive hydrogen bonding. It has been recently demonstrated that the combination of coordination and the sulfonate group has the capacity for formation of a strong supramolecular aggregate through hydrogen bonds, and it represents a new strategy for the design of second-harmonic generation materials (Xie *et al.*, 2002).

In (I), the ligands forming the dimer are stacked (pyridine–phenyl) one over another along the *a* axis. The centroid-to-centroid and interplanar distances are 3.456 (2) and 3.420 (5) Å, respectively, and the slip angle (the angle between the centroid vector and normal to the plane) is 9.06 (4)°. The supramolecular architecture (Fig. 2) is further stabilized by the variety of O—H⋯O hydrogen bonds involving the deprotonated quinolinol–O arom, the sulfonate O atoms, and uncoordinated and coordinated water molecules. One of the uncoordinated water molecules (O5W) bridges the quinolinolate–O atom (O1) and another water molecule (O4W) through a pair of O—H⋯O hydrogen bonds, where the water O atom (O5W) acts as a hydrogen-bond donor in both cases. Another water molecule (O4W) bridges the quinolinolate–O atom (O1) of one dimer and the axial water molecule (O2W) of another dimer *via* a pair of O—H⋯O hydrogen bonds, where this water O atom acts as a hydrogen-bond donor as well as an acceptor. The equatorial water molecule (O3W) bridges the two uncoordinated water molecules (O4W and O5W). The axial water molecule (O2W) bridges one of the sulfonate O atoms (O4) and a water molecule (O4W). The equatorial water molecule (O1W) is hydrogen bonded to two sulfonate O atoms (O2 and O4). The two uncoordinated water molecules (O4W and O5W) interact with each other to form a hydrogen-bonded ring with the graph-set motif $R_2^2(4)$ (Etter,
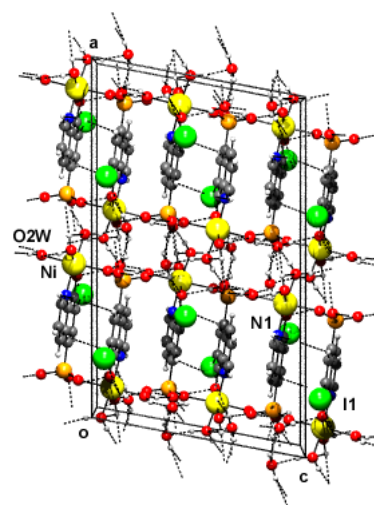

Figure 2
View, along the *b* axis, of the supramolecular architecture involving O—H⋯O hydrogen bonds.

1990; Bernstein *et al.*, 1995). The I atom is surrounded by five O atoms from neighbouring molecules at distances in the range 3.563 (9)–3.881 (7) Å (I···O van der Waals distance = 3.5 Å). The presence of halogen–oxygen interactions has been recognized in the literature and widely used in crystal engineering (Thalladi *et al.*, 1996). The various O—H···O hydrogen bonds forming the supramolecular network structure are listed in Table 2.

Experimental

Aqueous solutions of $Ni(NO_3)_2.6H_2O$ (0.145 g) and 7-iodo-8-hydroxyquinoline-5-sulfonic acid (Riedel-de-Haen, 0.175 g) were mixed in a 1:1 molar ratio. The resulting mixture was warmed over a water bath for half an hour and maintained at room temperature for crystallization. Green crystals appeared after a few days.

Crystal data

$[Ni(C_9H_4INO_6S)_2(H_2O)_6]\cdot4H_2O$	$D_x = 2.304$ Mg m^{-3}
$M_r = 995.74$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 10072
$a = 22.053$ (4) Å	reflections
$b = 10.009$ (2) Å	$\theta = 3.5$–$25.1°$
$c = 13.241$ (3) Å	$\mu = 3.69$ mm^{-1}
$\beta = 100.760$ (3)°	$T = 120$ (2) K
$V = 2871.3$ (10) Å^3	Cuboid, green
$Z = 4$	$0.35 \times 0.30 \times 0.20$ mm

Data collection

Kuma KM4CCD diffractometer	$R_{int} = 0.036$
ω scans	$\theta_{max} = 25.1°$
Absorption correction: multi-scan	$h = -26 \rightarrow 26$
(*XEMP*; Siemens, 1990)	$k = -11 \rightarrow 11$
$T_{min} = 0.236$, $T_{max} = 0.465$	$l = -15 \rightarrow 13$
10 398 measured reflections	5 standard reflections
2539 independent reflections	frequency: 60 min
2405 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.026$	independent and constrained
$wR(F^2) = 0.095$	refinement
$S = 0.83$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
2539 reflections	where $P = (F_o^2 + 2F_c^2)/3$
229 parameters	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.76$ e Å^{-3}
	$\Delta\rho_{min} = -0.94$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I1—C7	2.088 (4)	S1—O2	1.470 (3)
Ni—O1	2.039 (2)	S1—O3	1.465 (3)
Ni—O1W	2.070 (3)	S1—O4	1.455 (2)
Ni—O2W	2.088 (3)	S1—C5	1.771 (4)
Ni—O3W	2.020 (3)	O1—C8	1.318 (4)
Ni—N1	2.041 (3)	N1—C9	1.370 (5)
Ni—O3^i	2.162 (3)	N1—C2	1.316 (5)
O1—Ni—O1W	178.86 (10)	O1W—Ni—O3^i	91.59 (9)
O1—Ni—O2W	91.25 (11)	O2W—Ni—O3W	92.85 (11)
O1—Ni—O3W	94.53 (9)	O2W—Ni—N1	92.87 (11)
O1—Ni—N1	81.84 (11)	O2W—Ni—O3^i	177.09 (11)
O1—Ni—O3^i	88.35 (9)	O3W—Ni—N1	173.29 (11)
O1W—Ni—O2W	88.75 (11)	O3^i—Ni—O3W	84.30 (10)
O1W—Ni—O3W	84.33 (10)	O3^i—Ni—N1	89.93 (10)
O1W—Ni—N1	99.30 (11)	C2—N1—C9	119.7 (3)

Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H11···O2^{ii}	0.94 (4)	1.84 (4)	2.779 (4)	177 (5)
O1W—H12···O4^{iii}	0.95 (3)	2.15 (3)	3.027 (4)	155 (4)
O2W—H21···O4^{ii}	0.96 (4)	1.94 (4)	2.856 (4)	161 (3)
O2W—H22···O4W^{iv}	0.95 (4)	1.93 (4)	2.835 (4)	160 (4)
O3W—H31···O5W	0.95 (2)	1.86 (3)	2.768 (4)	160 (5)
O3W—H32···O4W	0.96 (5)	1.80 (5)	2.753 (4)	172 (4)
O4W—H41···O1^v	0.95 (4)	2.00 (4)	2.947 (4)	175 (4)
O4W—H42···O5W^v	0.94 (5)	1.93 (4)	2.746 (4)	143 (4)
O5W—H51···I1^v	0.93 (4)	2.96 (4)	3.555 (3)	123 (4)
O5W—H51···O1^v	0.93 (4)	2.04 (5)	2.916 (4)	156 (4)
O5W—H52···O4W^v	0.94 (4)	1.91 (4)	2.746 (4)	148 (5)
C2—H2···I1^{vi}	0.93	3.01	3.696 (4)	132
C4—H4···O3	0.93	2.60	3.156 (5)	119
C4—H4···O4W^{vii}	0.93	2.57	3.363 (5)	144
C6—H6···O4	0.93	2.45	2.862 (4)	107
C6—H6···I1^{viii}	0.93	3.02	3.751 (4)	136

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

All water H atoms were located from a difference map and were refined with fixed U_{iso} values. Aromatic H atoms were refined as riding.

Data collection: *KM*4 *CCD Software* (Kuma, 1999); cell refinement: *KM*4 *CCD Software*; data reduction: *KM*4 *CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXS*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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