Polymeric diaqua(μ-8-hydroxy-7-iodo-quinoline-5-sulfonato-κ^4N,O,O',O'')-copper(II) tetrahydrate

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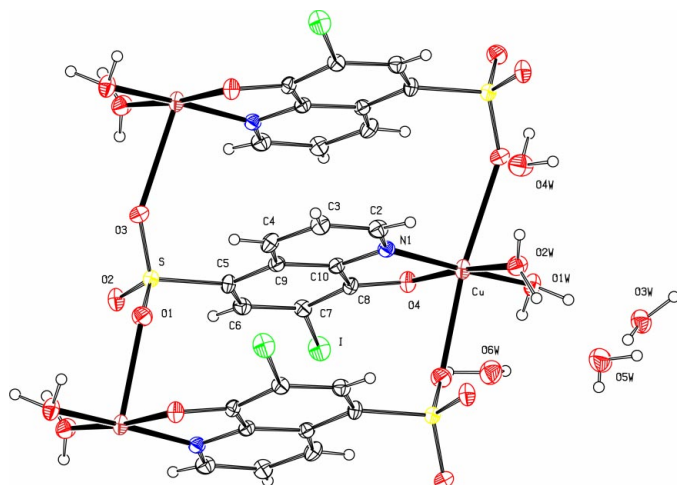In the title complex, $\{[Cu(C_9H_4INO_4S)(H_2O)_2]\cdot 4H_2O\}_n$, the coordination geometry around copper is distorted octahedral, the Cu atom being surrounded by two O atoms of the sulfonate group, N and O atoms of the oxine moiety (bidentate chelation) and two water molecules. The O atoms of the sulfonate group bridge the Cu atoms, leading to a polymeric ladder network. The copper ions and the sulfonate groups constitute the rails of the ladder and the oxine motifs act as the rungs. Channels of water molecules are present between these ladders.

Comment

The investigation of three-dimensional networks constructed by metal sulfonates through various modes of coordination is of current interest (Cai *et al.*, 2001; Onoda *et al.*, 2001; Cote *et al.*, 2002). 8-Hydroxyquinoline (oxine) and its derivatives are well known for their antifungal, antibacterial and anti-amoebic activities (Bambury, 1979). Oxine forms complexes with a large number of inorganic ions and so do most of its derivatives (Palenik, 1964; Hughes & Truter, 1977). In 8-hydroxyquinoline-5-sulfonic acid (HQS) the sulfonic acid group offers additional metal binding sites. In the crystal structure of a Cu complex of HQS, both dimeric and polymeric motifs have been observed (Petit, Ammor *et al.*, 1993; Petit, Coquerel *et al.*, 1993). In the Ni complex of HQS, only metal chelation by N and quinolinol O atoms has been observed and the O atoms of the sulfonate group are not involved in the coordination (Raj *et al.*, 2001). In the Na complex of HQS, all the O atoms of the sulfonate group are involved in coordination, along with bidentate chelation of the oxine ring (Raj *et al.*, 2002). The crystal structures of Ni (Raj *et al.*, 2003), Zn (Francis *et al.*, 2003) and Co (Balasubramanian, 1995) complexes of 8-hydroxy-7-iodoquinoline-5-sulfonate (ferron) have also been reported from our laboratory. They are isomorphous and have cage-like dimeric motifs. In the title complex, (I), the metal binding mode of the ligand is different from those in the other structures cited above.
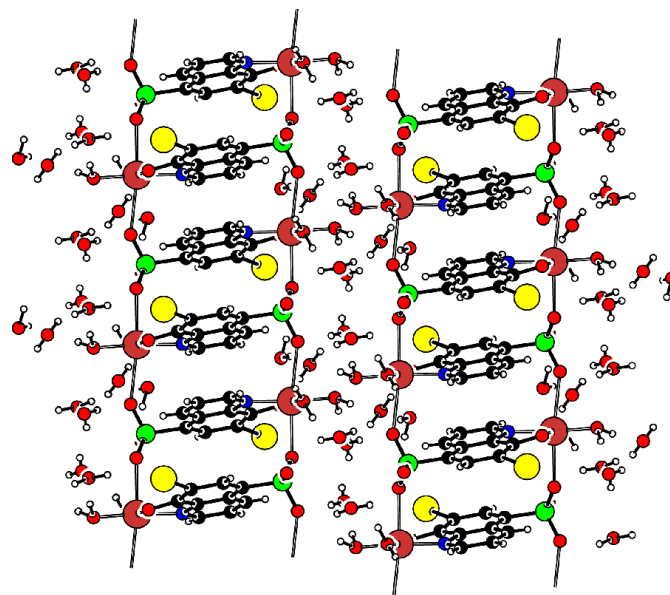

(I)
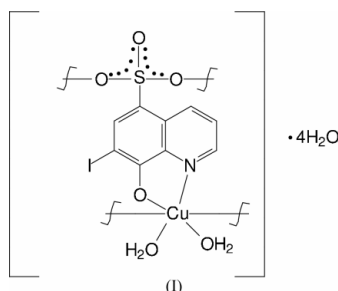
Figure 1
The polymeric network of complex (I). Ellipsoids are drawn at the 30% probability level.

Figure 2
Supramolecular ladders in complex (I).

The coordination geometry around copper is distorted octahedral. The Cu atom is surrounded by O atoms (O1 and O3) of two different sulfonate groups, N and O atoms (bidentate chelation) of the oxine moiety and two water molecules. The two O atoms of the sulfonate groups are in axial positions and the N and O atoms of the oxine ring and the water molecules occupy equatorial positions. The bond distances and angles (Table 1) agree with those of related copper complexes (Aller *et al.*, 2002; Ma *et al.*, 2003; Cai *et al.*, 2001). The O atoms of the sulfonate groups bridge the Cu atoms, leading to a polymeric ladder network, as shown in Fig. 1. In this polymeric ladder, neighbouring monomers are related by inversion centres. The copper ions and the sulfonate groups constitute the rails of the ladder and the oxine motifs act as the rungs. Channels of water molecules are present between these ladders (Fig. 2).

The coordinated water molecules O1W and O2W act as hydrogen-bond donors to the uncoordinated water molecules O3W and O5W, respectively. O5W also acts as an acceptor to O3W, forming an eight-membered [$R_3^1(8)$] ring. The sulfonate atom O3 acts as hydrogen-bond acceptor to the water molecule O5W, and O5W donates hydrogen to O6W. Furthermore, O6W acts as a hydrogen-bond acceptor to the coordinated water molecule O1W, forming a ten-membered hydrogen-bonded [$R_2^2(10)$] ring. Atoms O2W, O5W, O6W and sulfonate O3 are involved in hydrogen bonds, generating another ten-membered hydrogen-bonded [$R_3^3(10)$] ring. Water molecule O4W acts as an acceptor to the coordinated water molecule O2W and also acts as a hydrogen-bond donor to sulfonate atom O2, forming an eight-membered [$R_2^2(8)$] ring (Table 2).

The oxine rings are stacked over one another through π–π stacking interactions. The interplanar and centroid-to-centroid distances and the slip angle (defined as the angle between the plane normal and the line joining the centroids) are 3.380 Å, 3.591 Å and 17.7°, respectively. In this crystal structure, intermolecular I···O interactions [I···O2^{vi} =

3.3539 Å and I···O4W^{vii} = 3.6971 Å; symmetry codes: (vi) $1 - x$ $1 - y$, $-z$; (vii) $x, y - 1, z$] are observed. These types of halogen–oxygen interactions have also been observed in the crystal structures of ferron and its complexes (Balasubramanian & Muthiah, 1996; Raj *et al.*, 2003).

Experimental

Hot aqueous solutions of 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) (85 mg, Riedel de–Haen) and trimethoprim (73 mg, Shilpa Antibiotics Ltd) were mixed in a 1:1 molar ratio and warmed over a water bath for 1 h. On adding a hot aqueous solution of CuSO$_4$·5H$_2$O (62 mg, Merck) to the above solution, the colour changed from orange to green. The resulting mixture was warmed over a water bath for 1 h. The green precipitate was collected. Plate-shaped green crystals were recrystallized from an acetone–water (1:1) mixture.

Crystal data

[Cu(C$_9$H$_4$INO$_4$S)(H$_2$O)$_2$]·4H$_2$O	$D_x = 2.153$ Mg m^{-3}
$M_r = 520.75$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 14839
$a = 7.321$ (2) Å	reflections
$b = 9.682$ (3) Å	$\theta = 1.8–28.2°$
$c = 22.817$ (3) Å	$\mu = 3.46$ mm^{-1}
$\beta = 96.54$ (2)°	$T = 293$ (2) K
$V = 1606.8$ (7) Å^3	Plate, green
$Z = 4$	$0.34 \times 0.25 \times 0.15$ mm

Data collection

Bruker SMART CCD	3625 independent reflections
diffractometer	2847 reflections with $I > 2\sigma(I)$
ω–2θ scans	$R_{int} = 0.143$
Absorption correction: multi-scan	$\theta_{max} = 28.2°$
(*SADABS*; Bruker, 2001)	$h = -9 \rightarrow 9$
$T_{min} = 0.367$, $T_{max} = 0.594$	$k = -12 \rightarrow 12$
14839 measured reflections	$l = -29 \rightarrow 29$

Refinement

Refinement on F^2		H-atom parameters constrained	
$R[F^2 > 2\sigma(F^2)] = 0.041$		$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2]$	
$wR(F^2) = 0.090$		$(\Delta/\sigma)_{max} = 0.001$	
$S = 1.07$		$\Delta\rho_{max} = 0.75$ e Å^{-3}	
3625 reflections		$\Delta\rho_{min} = -1.60$ e Å^{-3}	
208 parameters			

Table 1
Selected geometric parameters (Å, °).

Cu—O1W	1.957 (3)	Cu—N1	1.982 (3)
Cu—O2W	1.966 (2)	Cu—O1^i	2.436 (3)
Cu—O4	1.963 (2)	Cu—O3^{ii}	2.615 (3)
O1W—Cu—O2W	90.94 (12)	O2W—Cu—O3^{ii}	81.06 (11)
O1W—Cu—O4	88.94 (11)	O4—Cu—N1	83.86 (11)
O1W—Cu—N1	171.62 (12)	O1^i—Cu—O4	79.15 (11)
O1^i—Cu—O1W	92.09 (11)	O3^{ii}—Cu—O4	104.59 (11)
O1W—Cu—O3^{ii}	82.20 (11)	O1^i—Cu—N1	90.76 (11)
O2W—Cu—O4	174.27 (13)	O3^{ii}—Cu—N1	95.45 (11)
O2W—Cu—N1	96.66 (12)	O1^i—Cu—O3^{ii}	173.04 (9)
O1^i—Cu—O2W	95.13 (11)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···O3W	0.80	1.93	2.719 (4)	169
O1W—H2W···O6W	0.80	1.92	2.720 (4)	175
O2W—H3W···O4W	0.82	1.88	2.684 (4)	170
O2W—H4W···O5W	0.80	2.09	2.866 (5)	161
O3W—H5W···O5W	0.79	1.97	2.750 (5)	171
O3W—H6W···O4^i	0.81	1.97	2.785 (4)	178
O4W—H7W···O3W^i	0.80	2.00	2.795 (4)	167
O4W—H8W···O2^{ii}	0.81	2.00	2.794 (4)	166
O5W—H9W···O6W^{iii}	0.81	2.12	2.899 (5)	162
O5W—H10W···O3^{iv}	0.90	2.08	2.975 (5)	173
O6W—H11W···O3^v	0.81	2.18	2.955 (4)	163

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

The H atoms of the aromatic groups were positioned geometrically and those of water molecules were obtained in difference Fourier map. All were treated as riding atoms, with C—H distances of 0.93 Å and O—H distances of 0.79–0.90 Å, with isotropic displacement parameters of 1.2 times U_{eq} of the parent atom. The deepest hole lies close to the I atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

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