organic compounds

Hydrogen-bonded supramolecular motifs in 4,4′-bipyridinium 8-hydroxy-7-iodoquinoline-5-sulfonate dihydrate

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In the title compound, $C_{10}H_9N_2^+ \cdot C_9H_5INO_4S^- \cdot 2H_2O$, the 4,4′-bipyridine molecule is protonated at one of the pyridine N atoms. These moieties self-assemble into a supramolecular chain along the a axis through $N-H\cdots N$ hydrogen bonds. The quinolinol OH group acts as a donor with respect to a sulfonate O atom $[O-H\cdots O(sulfonate)]$ and acts as an acceptor with respect to a $C-H$ group of ferron $[C-H\cdots O(hydroxy)]$, forming a supramolecular chain along the b axis. These two types of supramolecular chains (one type made up of bipyridine motifs and the other made up of sulfoxine motifs) interact via $\pi-\pi$ stacking, generating a three-dimensional framework. These chains are further crosslinked by $C-H\cdots O$ hydrogen bonds and $O-H\cdots O$ hydrogen bonds involving water molecules.

Comment

Derivatives of 8-hydroxyquinoline (oxine) are known for their antiamoebic, antibacterial and antifungal activities, which are correlated to their metal-chelating ability (Banerjee & Saha, 1986). The introduction of sulfonic acid into the oxine moiety offers additional metal-binding and hydrogen-bonding sites/modes. This type of ligand is called sulfoxine (sulfonic acid + oxine). Hydrogen bonds are primarily electrostatic and are formed with both strong and weak donors and acceptors (Desiraju & Steiner, 1999). The hydrogen-bonding patterns and metal-binding modes of sulfoxinates are of current interest (Cai, Chen, Liao et al., 2001; Cai, Chen, Feng et al., 2001). The crystal structures of 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron; Balasubramanian & Muthiah, 1996), a cobalt complex of ferron (Balasubramanian, 1995), a nickel(II) complex of ferron (Raj et al., 2003) and a zinc(II) complex of ferron (Francis et al., 2003) have recently been reported from our laboratory. 4,4′-Bipyridine is an excellent synthon for preparing novel supramolecular structures, owing

to its rigidity and aptness to form strong hydrogen bonds/coordination bonds via its two N atoms. Supramolecular structures made up of many 4,4′-bipyridine compounds have been reported (Lough et al., 2000). In this paper, the hydrogen-bonding patterns of 4,4′-bipyridinium 8-hydroxy-7-iodoquinoline-5-sulfonate dihydrate, (I), are discussed.


(I)
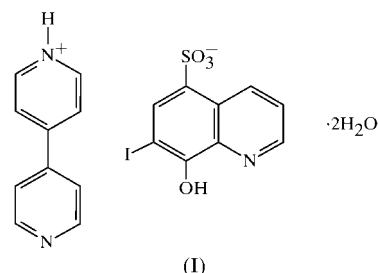
The asymmetric unit of (I) contains one 4,4′-bipyridinium cation, a 8-hydroxy-7-iodoquinoline-5-sulfonate (ferron) anion and two water molecules (Fig. 1). The bipyridine moiety is protonated at one of the ring N atoms (N1A), as is evident from the increase of the internal angle at nitrogen (C2A—N1A—C6A) from 115.45 (19)° in neutral 4,4′-bipyridine (Boag et al., 1999) to 121.5 (5)° in the present study. This increase of the internal angle has also been observed in many 4,4′-bipyridinium salts (Iyere et al., 2002). In the 4,4′-bipyridinium cation, the two rings are twisted by 31.05 (3)° about the C7A—C4A bond; this angle normally ranges from 17 (1) to 38.4 (9)° (Subbotin & Aslanov, 1986). The sulfonic acid group is deprotonated. In the 8-hydroxy-7-iodoquinoline system, the hydroxy H atom forms an intramolecular hydrogen bond with the quinoline N atom, leading to a hydrogen-bonded ring with graph-set notation $S(5)$, as is also observed in the neutral 8-hydroxyquinoline system. The quinolinol O1 atom is hydrogen bonded to the sulfonate O3 atom and the C4 atom of a screw-related ligand; atom C4 is also hydrogen bonded to the quinolinol oxygen (O1), forming a hydrogen-bonded ring with graph-set notation $R_2^2(8)$ (Etter, 1990; Bernstein et al., 1995). The 4,4′-bipyridinium moieties self-assemble into a supramolecular chain along the a axis through $N-H\cdots N$ hydrogen bonds involving the protonated and unprotonated N atoms. These two types of supramolecular chains (one type made up of bipyridine motifs and the other made up of sulfoxine motifs) interact via $\pi-\pi$ stacking, generating a three-dimensional framework. These chains are further crosslinked by $C-H\cdots O$ and $O-H\cdots O$ hydrogen bonds involving water molecules (Table 2 and Fig. 2). The various $O\cdots O$ interactions are as follows: $O1W\cdots O1W(-x + 1, -y, -z) = 2.8164 (7)$ Å, $O1W\cdots O2W(-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}) = 2.8113 (7)$ Å and $O2W\cdots O2W(-x + 2, -y + 1, -z + 1) = 2.7961 (8)$ Å.

In the structure of (I), $\pi-\pi$ interactions between the aromatic rings are observed. The N1/C2–C4/C9/C10 pyridine ring of ferron has stacking interactions with the N1A/C2A–C6A pyridine ring of the 4,4′-bipyridinium cation, with a perpendicular separation of 3.498 Å, a centroid-to-centroid distance of 3.653 (3) Å and a slip angle (the angle between the centroid vector and the normal to the plane) of 16.48°. The

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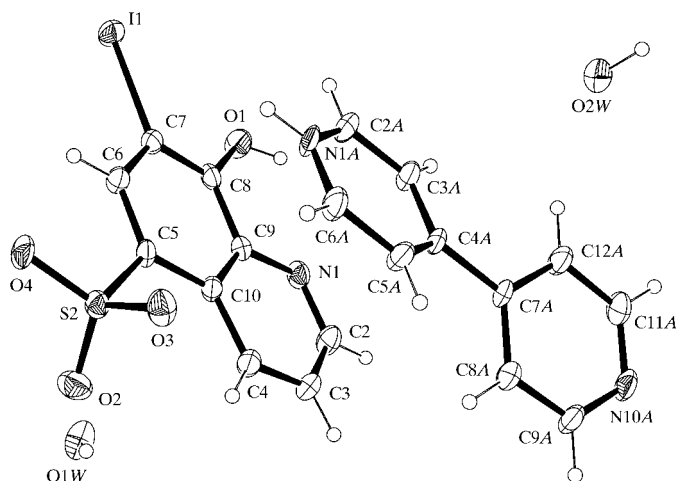
Figure 1
A view of the components of (I), with the atom-labelling scheme and 50% probability displacement ellipsoids.

C5–C10 phenyl ring of ferron is positioned over the N1A/ C2A–C6A pyridine ring of the 4,4′-bipyridinium cation, with a perpendicular separation of 3.521 Å, a centroid-to-centroid distance of 3.813 (3) Å and a slip angle of 31.23°. These values are close to those reported for aromatic π–π stacking inter-
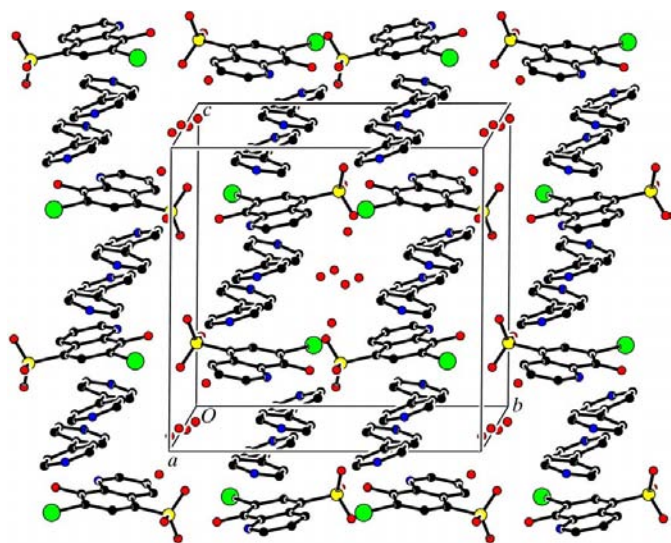
Figure 2
A view of the molecular packing, with H atoms omitted for clarity.

actions (Hunter, 1994). The I1 atom is in contact with the sulfonate O4 atom [I1···O4($-x$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$) = 3.105 (4) Å; van der Waals distance = 3.50 Å; C7—I1···O4 = 172.3 (18)°]; this I···O interaction was also observed in the crystal structure of ferron (Balasubramanian & Muthiah, 1996). This type of halogen–oxygen interaction has been recognized in the literature and is widely used in crystal engineering (Thalladi *et al.*, 1996).

Experimental

Hot aqueous solutions of 4,4′-bipyridine (39.05 mg) and ferron (87.80 mg) were mixed in a 1:1 molar ratio. The resulting solution was warmed over a water bath for half an hour and kept at room temperature for crystallization. After a few days, plate-shaped yellow crystals were obtained.

Crystal data

$C_{10}H_9N_2{}^+\cdot C_9H_5INO_4S^-\cdot 2H_2O$	Mo $K\alpha$ radiation
$M_r = 541.32$	Cell parameters from 25
Monoclinic, $P2_1/c$	reflections
$a = 9.657\ (3)$ Å	$\theta = 3.0$–27.0°
$b = 15.213\ (3)$ Å	$\mu = 1.69$ mm^{-1}
$c = 14.679\ (2)$ Å	$T = 293$ K
$\beta = 106.01\ (3)°$	Plate, yellow
$V = 2072.9\ (9)$ Å^3	$0.29 \times 0.20 \times 0.19$ mm
$Z = 4$	
$D_x = 1.735$ Mg m^{-3}	

Data collection

Philips PW1100 diffractometer	$k = 0 \rightarrow 19$
ω scans	$l = 0 \rightarrow 18$
4690 measured reflections	1 standard reflection
4526 independent reflections	every 100 reflections
3101 reflections with $I > 2\sigma(I)$	intensity decay: none
$R_{int} = 0.065$	
$\theta_{max} = 27.0°$	
$h = -12 \rightarrow 11$	

Table 1
Selected geometric parameters (Å, °).

I1—C7	2.091 (5)	N1—C9	1.360 (7)
S2—O2	1.438 (5)	N1—C2	1.313 (8)
S2—O3	1.454 (5)	N1A—C2A	1.326 (8)
S2—O4	1.454 (4)	N1A—C6A	1.332 (8)
S2—C5	1.789 (5)	N10A—C9A	1.341 (8)
O1—C8	1.353 (6)	N10A—C11A	1.330 (8)
O2—S2—O3	113.4 (3)	S2—C5—C10	121.0 (4)
O2—S2—O4	113.4 (3)	I1—C7—C8	121.2 (3)
O2—S2—C5	105.3 (3)	I1—C7—C6	119.3 (4)
O3—S2—O4	112.7 (3)	O1—C8—C7	120.0 (5)
O3—S2—C5	105.7 (3)	O1—C8—C9	119.7 (5)
O4—S2—C5	105.5 (3)	N1—C9—C8	116.2 (4)
C2—N1—C9	117.3 (5)	N1—C9—C10	123.4 (5)
C2A—N1A—C6A	121.5 (5)	N1A—C2A—C3A	120.6 (5)
C9A—N10A—C11A	118.2 (5)	N1A—C6A—C5A	120.5 (5)
N1—C2—C3	124.3 (6)	N10A—C9A—C8A	122.5 (6)
S2—C5—C6	119.0 (4)	N10A—C11A—C12A	122.9 (6)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.82	2.30	2.688 (6)	110
O1—H1···O3^i	0.82	2.18	2.837 (7)	137
N1A—H1A···N10A^{ii}	0.86	1.80	2.662 (6)	178
O1W—H11W···O2	0.94	2.10	2.856 (6)	137
O2W—H22W···O4^{iii}	0.94	1.99	2.864 (6)	153
C3A—H3A···O2^i	0.93	2.44	3.283 (8)	152
C4—H4···O1^{iv}	0.93	2.50	3.388 (7)	159
C6—H6···O4	0.93	2.43	2.850 (7)	108
C12A—H12A···O2W	0.93	2.43	3.321 (9)	160

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

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Atom H11*W* of water molecule O1*W* and atom H22*W* of water molecule O2*W* were located from a difference Fourier map and allowed for but not refined in subsequent calculations. The remaining H atom of each water molecule could not be located. All other H atoms were refined using a riding model; U_{iso} values were set at 1.2U_{eq}(parent).

Data collection: *FEBO* (Belletti, 1996); cell refinement: *MolEN* (Fair, 1990); data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*97 (Spek, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1227). Services for accessing these data are described at the back of the journal.

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