

Savarimuthu Baskar Raj,^a
Packianathan Thomas
Muthiah,^{a*} Gabriele Bocelli^b and
Andrea Cantoni^b^aDepartment of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, Tamilnadu, India, and ^bIMEM-CNR, Palazzo Chimico Campus, Parco Area delle Scienze, 17/a, I-43100, ItalyCorrespondence e-mail:
tommtrichy@yahoo.co.in

Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(C-C)$ = 0.003 Å
R factor = 0.061
wR factor = 0.174
Data-to-parameter ratio = 17.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

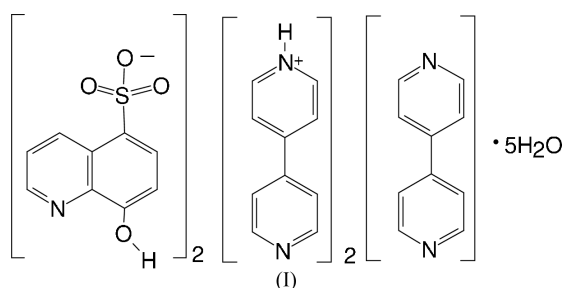
Bis(4,4'-bipyridinium) bis(8-hydroxyquinoline-5-sulfonate) bipyridine pentahydrate

In the title compound, $2C_{10}H_9N_2^+ \cdot 2C_9H_6SO_4^- \cdot C_{10}H_8N_2 \cdot 5H_2O$, the asymmetric unit contains two 8-hydroxyquinoline-5-sulfonate (HQS) anions, two 4,4'-bipyridinium ions, a neutral 4,4'-bipyridine molecule and five water molecules. The sulfonic acid group is deprotonated. Interestingly, in both the HQS anions, the O–H bond is oriented away from the quinoline-N atom, since the water molecule competes in hydrogen bonding with the quinolinol-O atom. The neutral 4,4'-bipyridine and one of the protonated 4,4'-bipyridine moieties are bridged by two water molecules, resulting in a 'U'-shaped hydrogen-bonded molecular arrangement. Many stacking interactions were observed between: (i) the pyridine rings of bipyridine moieties; (ii) the pyridine rings of bipyridine and HQS moieties; (iii) the pyridine ring of bipyridine and the benzene ring of the HQS anion.

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Comment

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



offers additional metal binding and hydrogen-bonding sites/modes. This type of ligand is called sulfoxine (SULFonic acid + OXINE). Hydrogen-bonding patterns involving aryl sulfonates and their metal complexes are of contemporary interest (Cai, Chen, Liao, Feng & Chen, 2001; Cai, Chen, Liao, Yao *et al.*, 2001; Cai, Chen, Feng *et al.*, 2001; Onoda *et al.*, 2001). Hydrogen-bonding patterns of sulfoxines (Balasubramanian & Muthiah, 1996*a,b*) and metal sulfoxinates (Baskar Raj *et al.*, 2001, 2002, 2003; Francis *et al.*, 2003; Murugesan & Muthiah, 1997) have also been reported from our laboratory. In the

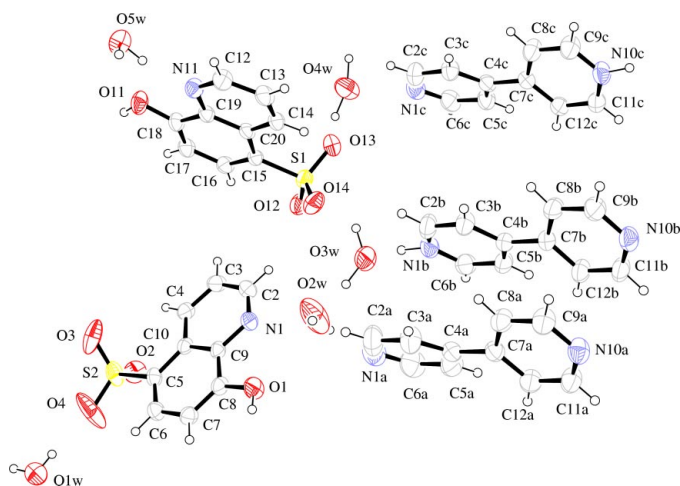


Figure 1

A view of the asymmetric unit of (I) with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

course of our efforts to prepare a mixed-ligand complex of sodium involving 8-hydroxyquinoline-5-sulfonic acid and 4,4'-bipyridine, which have been extensively used as building units in the crystal engineering of many supramolecular structures (Dong *et al.*, 2002; Fu *et al.*, 2000), we obtained the title complex, (I).

The bond lengths and angles in (I) (Fig. 1) are normal (Table 1). The asymmetric unit contains two 8-hydroxyquinoline-5-sulfonate anions, two 4,4'-bipyridinium ions, a neutral 4,4'-bipyridine and five water molecules. Two 4,4'-bipyridine moieties are protonated at one of the ring N atoms (N1b and N10c), as is evident from the increase of the internal angle at N to 121° from 115.8° in neutral 4,4'-bipyridine (Boag *et al.*, 1999). Although the literature is replete with the crystal structures of the 4,4'-bipyridinium dication with a variety of anions and alkyl substituents, structural details for the monoprotonated cation are scarce (Iyere *et al.*, 2002). The range of values for the angles at the N atom (neutral motifs) of the bipyridine molecules [116.1 (3)–117.6 (2)°] compares well with the average value of 116.5° reported for neutral 4,4'-bipyridine molecules retrieved from the Cambridge Structural Database (CSD, Version 5.24; Allen, 2002). Similarly, the range of values for the angle at protonated N atoms of the 4,4'-bipyridine molecules [N1b 121.4 (2)° and N10c 120.3 (2)°] agrees well with the average CSD value of 121.5°. The dihedral angle between the two pyridyl planes of the neutral 4,4'-bipyridine molecule is 29.95 (15)°. The corresponding values for the two cations are 21.14 (13) and 25.34 (13)°, respectively.

The sulfonic acid group is deprotonated. The mean plane of the quinoline nucleus of one HQS anion makes a dihedral angle of 87.74 (7)° with that of the other HQS anion. In neutral 8-hydroxyquinoline systems, the H atom of the OH group makes an intramolecular hydrogen bond with the quinoline N atom leading to a hydrogen-bonded ring (see 2a in Fig. 2). In protonated 8-hydroxyquinoline systems (Balasubramanian & Muthiah, 1996*a, b*), the H atom of the OH

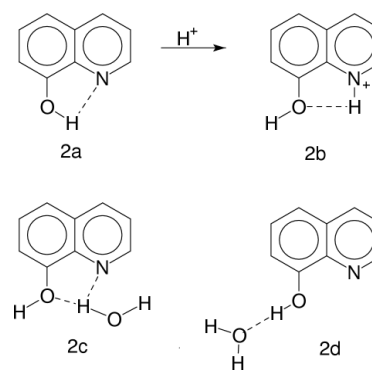


Figure 2

Schematic representation of hydrogen-bonding patterns in oxine systems.

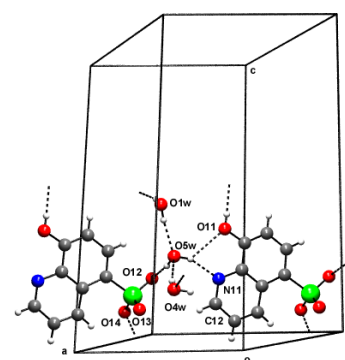


Figure 3

View of the packing, showing how the water molecule (O5W) interacts with two HQS moieties and two other water molecules.

group points away from the N atom (see 2b in Fig. 2). However, in both of the HQS anions of (I), the water molecules compete in the hydrogen bonding, leading to the OH bond pointing away from the N atom. In one of the HQS anion, a water H atom bridges the quinolinol O and N atoms, leading to a hydrogen-bonded chelation (with the graph-set notation $R_1^2(5)$ (see 2c in Fig. 2). Another H atom is bonded to the symmetry-related sulfonate–O atom (O12). Also, this water molecule accepts an H atom from atoms O1w and O4w. Thus, the water molecule (O5w) interacts with two HQS anions and two water molecules (Fig. 3). For the other HQS anion, the OH group is hydrogen bonded with water molecule O1w (see 2d in Fig. 2). One of the cations and the neutral bipyridine molecule are bridged by two water molecules (O3w and O2w), leading to a 'U'-shaped hydrogen-bonded molecular motif (Fig. 1). The vicinal atoms C8b and C9b of one of the protonated bipyridine moieties are hydrogen bonded to the symmetry-related water molecules (O1w). Details of the hydrogen-bonding interactions are given in Table 2.

There are many stacking interactions: (i) between the pyridine rings of bipyridine moieties [range of values for centroid-to-centroid distances = 3.68 (2)–3.83 (2) Å, interplanar distances = 3.40 (4)–3.72 (2) Å and slip angles = 12.2 (1)–23.9 (1)°], (ii) between the pyridine rings of bi-

pyridine and HQS moieties [range of centroid-to-centroid distances = 3.76 (2)–3.77(2) Å, interplanar distances = 3.32 (7)–3.55 (1) Å and slip angles = 24.5 (3)–29.0 (1)°], (iii) between the pyridine ring of bipyridine and the benzene ring of the HQS anions [range of centroid-to-centroid distances = 3.49 (2)–3.90 (2) Å, interplanar distances = 3.40 (6)–3.70 (9) Å and slip angles = 12.2 (9)–28.7 (6)°].

Experimental

Compound (I) was obtained while attempting to prepare a mixed-ligand complex of sodium involving 8-hydroxyquinoline-5-sulfonic acid and 4,4'-bipyridine. An aqueous solution of 4,4'-bipyridine (0.078 g) and an aqueous solution of 8-hydroxyquinoline-5-sulfonic acid monohydrate (0.122 g) were mixed in a 1:1 ratio. To this mixture, an aqueous solution of sodium sulfate (0.071 g) was added. The resultant mixture was warmed over a water bath for an hour and kept at room temperature for crystallization. Pale yellow crystals appeared after a few days.

Crystal data

$2C_{10}H_9N_2^+ \cdot 2C_9H_6SO_4^- \cdot C_{10}H_8N_2 \cdot 5H_2O$	$Z = 2$
$M_r = 1009.08$	$D_x = 1.432 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.449 (3) \text{ \AA}$	Cell parameters from 50 reflections
$b = 14.330 (2) \text{ \AA}$	$\theta = 1.1\text{--}30.5^\circ$
$c = 19.449 (3) \text{ \AA}$	$\mu = 0.19 \text{ mm}^{-1}$
$\alpha = 111.080 (2)^\circ$	$T = 293 \text{ K}$
$\beta = 93.730 (3)^\circ$	Plate, pale yellow
$\gamma = 104.770 (2)^\circ$	$0.33 \times 0.31 \times 0.21 \text{ mm}$
$V = 2339.9 (9) \text{ \AA}^3$	

Data collection

Bruker AXS SMART CCD diffractometer	12 128 independent reflections
ω scans	7325 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.055$
$T_{\text{min}} = 0.921$, $T_{\text{max}} = 0.958$	$\theta_{\text{max}} = 30.5^\circ$
29 740 measured reflections	$h = -13 \rightarrow 13$
	$k = -20 \rightarrow 20$
	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.061$	$w = 1/[\sigma^2(F_o^2) + (0.0967P)^2]$
$wR(F^2) = 0.174$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{\text{max}} = 0.001$
12 128 reflections	$\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$
688 parameters	$\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

S1—O12	1.4413 (19)	S2—O2	1.432 (2)
S1—O13	1.444 (2)	S2—O3	1.451 (2)
S1—O14	1.442 (2)	S2—O4	1.437 (3)
O12—S1—O13	112.76 (12)	O3—S2—O4	114.46 (17)
O12—S1—O14	112.21 (12)	O2—S2—O3	112.16 (13)
O13—S1—O14	113.37 (11)	O2—S2—O4	112.14 (17)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1 \cdots O4W ⁱ	0.82	1.77	2.574 (3)	168
N1B—H1B \cdots O3W ⁱⁱ	0.86	1.73	2.584 (3)	172
N10C—H10C \cdots N10A ⁱⁱⁱ	0.86	1.86	2.717 (3)	177
O1W—H11 \cdots O5W ⁱⁱⁱ	0.88	1.93	2.802 (3)	174
O11—H11' \cdots N10B ^{iv}	0.82	1.89	2.690 (2)	165
O1W—H12 \cdots O4 ^v	0.84	1.96	2.796 (4)	176
O2W—H21 \cdots O1	0.82	2.58	2.991 (3)	113
O2W—H22 \cdots N1A ^{vi}	0.81	2.15	2.790 (4)	136
O3W—H31 \cdots O2W	0.88	1.73	2.580 (4)	164
O3W—H32 \cdots O14 ^{vii}	0.86	1.83	2.679 (3)	171
O4W—H41 \cdots N1C ⁱⁱ	0.83	1.97	2.792 (3)	170
O4W—H42 \cdots O5W	0.84	1.91	2.736 (3)	167
O5W—H51 \cdots O11	0.99	2.45	3.153 (3)	127
O5W—H51 \cdots N11	0.99	1.82	2.761 (3)	158
O5W—H52 \cdots O12 ^{viii}	0.86	2.00	2.848 (3)	169
C8B—H8B \cdots O1W ^{viii}	0.93	2.46	3.312 (4)	152
C9B—H9B \cdots O1W ^{ix}	0.93	2.55	3.425 (4)	156
C12C—H12C \cdots O12 ^{viii}	0.93	2.29	3.210 (3)	171

Symmetry codes: (i) $x, y-1, z$; (ii) $1-x, 1-y, -z$; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, 2-y, 1-z$; (v) $x-1, y, z$; (vi) $1-x, -y, -z$; (vii) $1+x, y, z$; (viii) $-x, 1-y, 1-z$; (ix) $x, 1+y, z$.

Water H atoms were located in a difference Fourier map. All H atoms were refined as riding [C—H = 0.93 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$, N—H = 0.81–0.99 Å and $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O})$, and N—H = 0.86 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{N})$].

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 1997); software used to prepare material for publication: PLATON (Spek, 1997).

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