organic papers

4,4'-Bipyridinium disaccharinate dihydrate

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The asymmetric unit of the title compound [systematic name: 4,4'-bipyridinium bis(2,3-dihydro-1,1,3-trioxo-1,2-benzothiazolate) dihydrate], $C_{10}H_{10}N_2^{2+} \cdot 2C_7H_4NO_3S^- \cdot 2H_2O$, consists of one half of a 4,4'-bipyridinium cation, which has inversion symmetry, one saccharinate anion and one water molecule. These ions and molecules are further linked into a supramolecular structure by intermolecular hydrogen bonds.

Comment

Hydrogen bonds and intermolecular interactions are widely used in organic crystal engineering to design and synthesize one-, two- and three-dimensional supramolecular networks (Beatty, 2003). 4,4'-Bipyridine is an excellent synthon in preparing novel structures, owing to its rigidity and its ability to form strong hydrogen bonds or coordination bonds *via* its two N atoms. Many supramolecular architectures involving 4,4'-bipyridine have been reported (Lough *et al.*, 2000). We report here the crystal structure of the title complex salt, (I), consisting of a complex cation, 4,4'-bipyridinium, two saccharinate (2,3-dihydrooxobenzisosulfonazolate) anions and two water molecules.

(I)
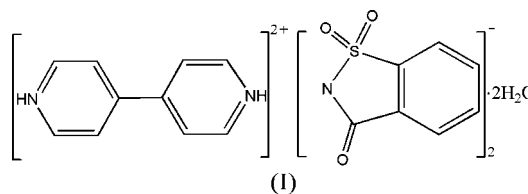
The asymmetric unit of (I) (Fig. 1) contains one half of a 4,4'-bipyridinium cation, one saccharinate anion and one water molecule. 4,4'-Bipyridine is protonated on both N atoms, as is evident from the increase in the internal angle [C8—N2—C12 increases from 115.45 (19)° in neutral 4,4-bipyridine (Boag *et al.*, 1999) to 121.1 (2)° in (I)]. Such an increase in the internal angle has also been observed in many 4,4'-bipyridinium salts (Iyere *et al.*, 2002). The 4,4'-bipyridinium cation lies on an inversion centre (Fig. 1). The saccharinate ion is essentially planar, with an r.m.s. deviation of 0.03 (1) Å, and the bond geometry of the saccharinate ion is similar to those of reported complexes containing saccharinate as the counter-ion (Deng *et al.*, 2000; Topcu *et al.*, 2001; Yilmaz, Andac *et al.*, 2001; Yilmaz, Topcu *et al.*, 2001; Yilmaz, Yilmaz *et al.*, 2001).

These ions and the water molecules are further linked together by intermolecular N—H···O, O—H···N, O—H···O and C—H···O hydrogen bonds (Fig. 2 and Table 1).
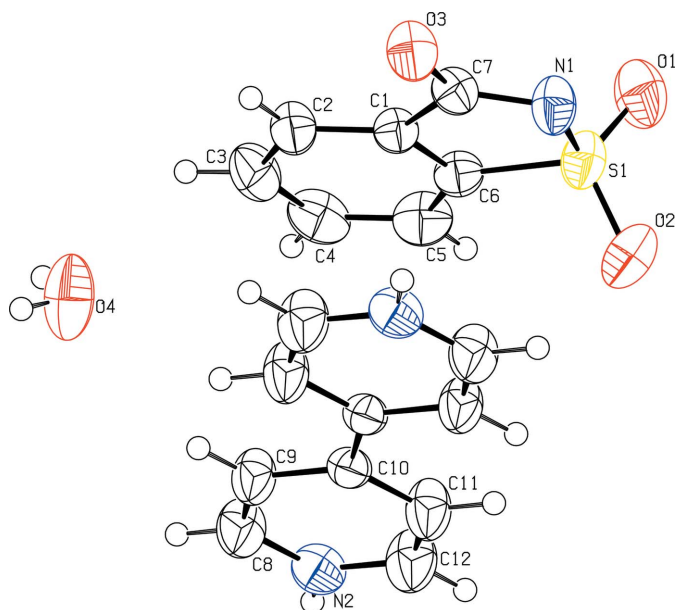
Figure 1
The structure of (I), with the atomic numbering of the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms are related to labelled atoms by the symmetry code $(-x, -y, -z)$.

Experimental

All reagents were commercially available and of analytical grade. An ethanol solution (5 ml) of 4,4′-bipyridine (1 mmol, 0.156 g) was added dropwise to a vigorously stirred solution of saccharin (2.0 mmol, 0.376 g) in distilled water (15 ml). The solution was stirred for 15 min with the temperature maintained at less than 353 K and then filtered. After 7 d, colourless crystals of (I) were obtained from the filtrate.
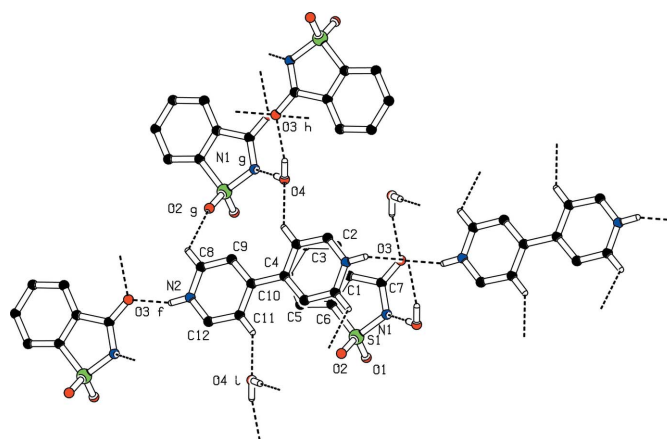
Crystal data

$C_{10}H_{10}N_2^{2+}·2C_7H_4NO_3S^−·2H_2O$	$V = 616.7 (2) \text{ Å}^3$
$M_r = 558.58$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.504 \text{ Mg m}^{-3}$
$a = 8.3215 (19) \text{ Å}$	Mo $K\alpha$ radiation
$b = 8.538 (2) \text{ Å}$	$\mu = 0.27 \text{ mm}^{-1}$
$c = 9.629 (2) \text{ Å}$	$T = 292 (2) \text{ K}$
$\alpha = 94.368 (4)°$	Block, colourless
$\beta = 102.874 (4)°$	$0.20 \times 0.10 \times 0.10 \text{ mm}$
$\gamma = 110.281 (4)°$	

Data collection

Bruker SMART CCD area-detector diffractometer	4792 measured reflections
φ and ω scans	2391 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	1777 reflections with $I > 2\sigma(I)$
$T_{min} = 0.947$, $T_{max} = 0.973$	$R_{int} = 0.028$
	$\theta_{max} = 26.0°$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.056$	
$wR(F^2) = 0.154$	$w = 1/[\sigma^2(F_o^2) + (0.0894P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	
2391 reflections	$(\Delta/\sigma)_{max} < 0.001$
184 parameters	$\Delta\rho_{max} = 0.44 \text{ e Å}^{-3}$
	$\Delta\rho_{min} = -0.39 \text{ e Å}^{-3}$

Figure 2
A view of part of the crystal structure of (I), showing hydrogen-bonding interactions (dashed lines). H atoms not involved in these contacts have been omitted for clarity.

Table 1
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N2—H1′$\cdots$O3[i]	0.86 (2)	1.81 (2)	2.642 (3)	163 (3)
O4—H41$\cdots$N1[ii]	0.86 (3)	2.05 (3)	2.913 (3)	176 (4)
O4—H42$\cdots$O3[iii]	0.85 (3)	2.00 (3)	2.838 (3)	168 (3)
C8—H8$\cdots$O2[ii]	0.93	2.56	3.154 (4)	122
C11—H11$\cdots$O4[iv]	0.93	2.29	3.095 (4)	144

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

All carbon-bound H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms bound to O and N were located in a difference map and refined, with their O—H and N—H distances restrained to 0.85 (2) and 0.86 (1) Å, respectively.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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