

## Hydrogen-bonding patterns in 4,4'-bipyridinium bis(3-carboxy-4-hydroxybenzenesulfonate) dihydrate

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## Key indicators

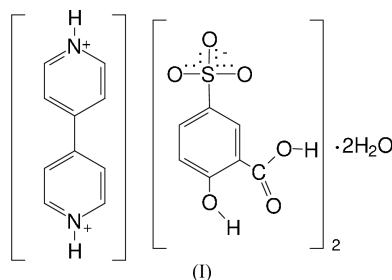
Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$   
 $R$  factor = 0.047  
 $wR$  factor = 0.131  
Data-to-parameter ratio = 12.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound,  $\text{C}_{10}\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{C}_7\text{H}_5\text{O}_6\text{S}^- \cdot 2\text{H}_2\text{O}$ , 4,4'-bipyridine is centrosymmetric and protonated at both N atoms. The inversion-related hydrogen-bonded supramolecular chains (made up of water molecules and sulfonate motifs arranged in an alternating manner) are cross-linked by 4,4'-bipyridinium cations *via*  $\text{N}-\text{H} \cdots \text{O}$  (sulfonate) hydrogen bonds.

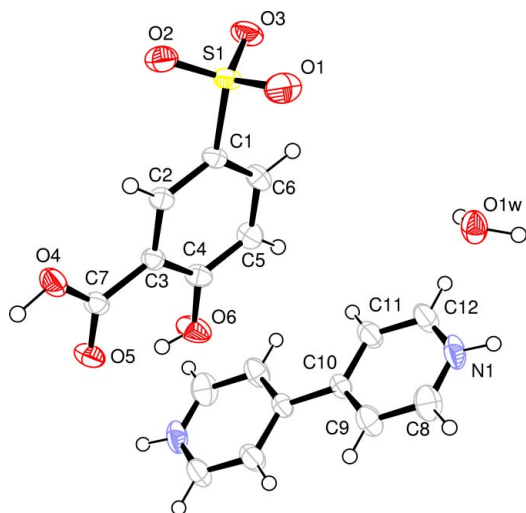
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## Comment

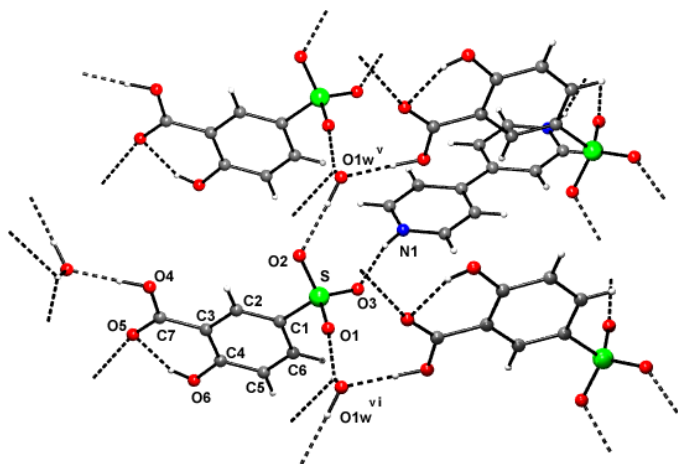
4,4'-Bipyridine is an excellent synthon in preparing novel structures, owing to its rigidity and ability to form strong hydrogen bonds/coordination bonds *via* its two N atoms. Many supramolecular architectures involving 4,4'-bipyridine have been reported (Lough *et al.*, 2000). Diprotonated 4,4'-bipyridinium cations have been used in the stabilization of molybdenum oxide layers (Zapf *et al.*, 1997) and the isolation of a new anionic lead iodide chain structure (Chakravarthy & Guloy, 1997). The crystal structure of 4,4'-bipyridine itself has been reported (Boag *et al.*, 1999). The crystal structures of 4,4'-bipyridine dihydrate (Näther *et al.*, 2001), dinitrate (Cooney *et al.*, 1990) and diiodide salts (Iyere *et al.*, 1998) have also been reported. Hydrogen-bonding patterns involving sulfonate groups in biological systems and metal complexes are of current interest (Onoda *et al.*, 2001). Such interactions can be utilized for designing supramolecular architectures (Baskar Raj *et al.*, 2003). The crystal structure of five transition metal (Mn, Co, Ni, Zn and Cu) complexes of the sulfosalicylate ion (3-carboxy-4-hydroxybenzenesulfonate) have been reported (Ma *et al.*, 2003*a,b,c,d,e*). The present study has been aimed at understanding the hydrogen-bonding patterns in the title compound, (I).



The asymmetric unit of (I) contains one-half of the centrosymmetric 4,4'-bipyridinium cation, one sulfosalicylate anion and a water molecule (Fig. 1 and Table 1). 4,4'-Bipyridine is protonated at atom N1 of the pyridine moiety, as evident from the increase in the internal angle  $[\text{C}8-\text{N}1-\text{C}12]$  increases from  $115.45(19)^\circ$  in neutral 4,4'-bipyridine (Boag *et*



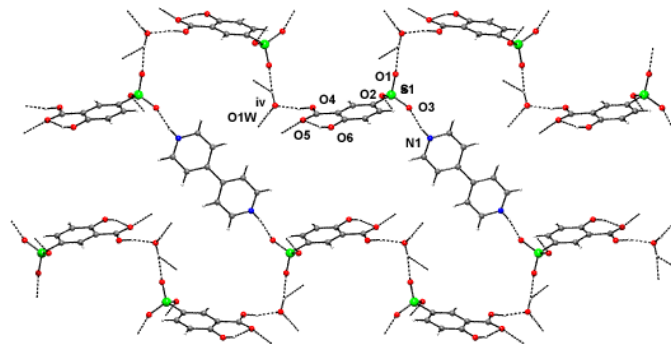
**Figure 1**  
A view of (I), with the atom-labelling scheme and 50% probability displacement ellipsoids.



**Figure 2**  
A view of the pivotal role of the water molecule in the hydrogen-bonding network. [Symmetry codes: (v)  $x - 1, \frac{1}{2} - y, z + \frac{1}{2}$ ; (vi)  $x, \frac{1}{2} - y, z + \frac{1}{2}$ ]

*al.*, 1999) to  $121.9(2)^\circ$  in (I)]. The increase of the internal angle has also been observed in many 4,4'-bipyridinium salts (Iyere *et al.*, 2002). The commonly observed intramolecular hydrogen bond between the phenol OH and carboxyl groups in salicylic acid is also present in the sulfosalicylate anion (Panneerselvam *et al.*, 2002).

In the hydrogen-bonding network (Table 2), the water molecule plays a pivotal role, as shown in Fig. 2. The water molecule bridges three 3-carboxy-4-hydroxy-benzene-sulfonate ions. It acts as a hydrogen-bond donor to two sulfonate groups [O1(sulfonate)  $\cdots$  H—O—H  $\cdots$  O2(sulfonate)], thus forming a hydrogen-bonded supramolecular chain of sulfonates. The inversion-related chains are linked by 4,4'-bipyridinium cations *via* N1—H1  $\cdots$  O3(sulfonate) hydrogen bonds, as shown in Fig. 3. Thus all three sulfonate O atoms act as hydrogen-bond acceptors. The water molecule also acts as an acceptor in hydrogen bonds with the carboxyl group. The carboxyl group does not form a hydrogen-bonded cyclic dimer



**Figure 3**  
A view of the linking *via* 4,4'-bipyridinium cations. [Symmetry codes: (iv)  $1 - x, -y, 1 - z$ .]

but rather acts as a hydrogen-bond donor to the water molecules. This type of preference and competition of hydrogen-bond acceptors for the strong carboxyl donor has also been reported in a database study (Steiner, 2001). A  $\pi$ - $\pi$  interaction is observed between two sulfosalicylate moieties related by an inversion centre. The centroid-to-centroid and interplanar distances are 3.943 and 3.408 Å, respectively, and the slip angle (the angle between the centroid vector and the normal to the plane) is  $30.2^\circ$ .

## Experimental

A hot aqueous solution of 4,4'-bipyridine (39.05 mg) and a hot aqueous solution of sulfosalicylic acid (54.52 mg) were mixed in 1:1 molar ratio. The resultant mixture was warmed over a water bath for half an hour and kept at room temperature for crystallization. After a few days, plate-like colourless crystals of (I) were obtained.

### Crystal data

$C_{10}H_{10}N_2^{2+} \cdot 2C_7H_5O_6S^- \cdot 2H_2O$   
 $M_r = 628.59$   
 Monoclinic,  $P2_1/c$   
 $a = 7.086(2) \text{ \AA}$   
 $b = 16.669(3) \text{ \AA}$   
 $c = 10.915(3) \text{ \AA}$   
 $\beta = 98.13(3)^\circ$   
 $V = 1276.3(6) \text{ \AA}^3$   
 $Z = 2$

$D_x = 1.636 \text{ Mg m}^{-3}$   
 Cu  $K\alpha$  radiation  
 Cell parameters from 50 reflections  
 $\theta = 4.9\text{--}69.9^\circ$   
 $\mu = 2.62 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Block, colourless  
 $0.31 \times 0.23 \times 0.17 \text{ mm}$

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.477, T_{\max} = 0.638$   
 2541 measured reflections  
 2418 independent reflections  
 2126 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$   
 $\theta_{\text{max}} = 69.9^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -4 \rightarrow 20$   
 $l = 0 \rightarrow 13$   
 1 standard reflection every 100 reflections  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.131$   
 $S = 1.09$   
 2418 reflections  
 200 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.59 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.97 \text{ e \AA}^{-3}$

**Table 1**  
Selected geometric parameters (Å, °).

S1—C1	1.7676 (19)	O5—C7	1.230 (2)
S1—O3	1.4595 (15)	O6—C4	1.356 (2)
S1—O1	1.4520 (16)	N1—C8	1.326 (3)
S1—O2	1.4592 (16)	N1—C12	1.334 (3)
O4—C7	1.316 (2)		
O2—S1—C1	106.75 (9)	N1—C12—C11	120.1 (2)
O3—S1—C1	105.91 (9)	S1—C1—C6	119.79 (14)
O1—S1—C1	106.60 (9)	S1—C1—C2	120.56 (14)
O1—S1—O2	112.48 (10)	O6—C4—C3	122.94 (17)
O1—S1—O3	111.87 (10)	O6—C4—C5	116.93 (17)
O2—S1—O3	112.66 (9)	O4—C7—O5	122.91 (17)
C8—N1—C12	121.9 (2)	O4—C7—C3	114.53 (16)
N1—C8—C9	120.2 (2)	O5—C7—C3	122.56 (18)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O3 <sup>i</sup>	0.88	1.84	2.698 (3)	165
O1W—H1W...O2 <sup>i</sup>	0.92	1.85	2.763 (2)	173
O1W—H2W...O5 <sup>ii</sup>	0.91	2.57	3.173 (2)	124
O1W—H2W...O1 <sup>iii</sup>	0.91	1.95	2.762 (2)	147
O4—H4...O1W <sup>iv</sup>	0.93	1.66	2.576 (2)	167
O6—H6A...O5	0.80	1.88	2.620 (2)	152
C2—H2...O2	0.93	2.56	2.932 (2)	104
C9—H9...O2 <sup>iv</sup>	0.93	2.52	3.379 (3)	153
C12—H12...O5 <sup>ii</sup>	0.93	2.42	3.217 (3)	143

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

The H atoms of the aromatic groups were positioned geometrically and those of the water molecule were positioned from difference Fourier maps. All H atoms were treated as riding. The C—H, O—H and N—H bond lengths are 0.93, 0.80–0.93 and 0.88 Å, respectively ( $U_{\text{iso}} = 1.2U_{\text{eq}}$ ).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; 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*.

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