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Bis(4-hydroxypyridinium) sulfate monohydrate

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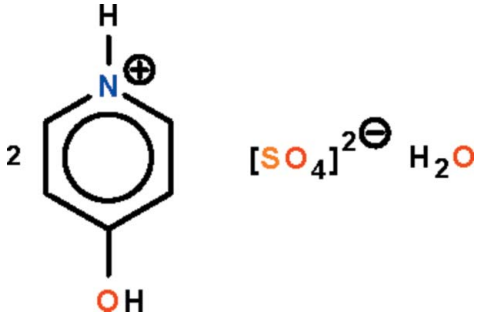
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.103; data-to-parameter ratio = 15.4.

In the crystal structure of the title salt, $2C_5H_6NO^+\cdot SO_4^{2-}\cdot H_2O$, one planar (r.m.s. deviation = 0.01 Å) cation is stacked approximately over the other [dihedral angle between planes = 8.6 (1)°]. The pyridinium and hydroxy H atoms are hydrogen-bond donor atoms to the O atoms of the sulfate anion; the cations, anions and water molecules are consolidated into a three-dimensional network through O—H···O and N—H···O hydrogen bonds.

Related literature

For the crystal structures of 4-hydroxypyridinium salts, see: Fukunaga *et al.* (2004); Gao *et al.* (2004); Kiviniemi *et al.* (2001); Wang *et al.* (2006).



Experimental

Crystal data

$2C_5H_6NO^+\cdot SO_4^{2-}\cdot H_2O$
M_r = 306.29
Monoclinic, $P2_1/n$
a = 7.1404 (2) Å
b = 19.9797 (5) Å
c = 9.5148 (2) Å
β = 102.557 (1)°
V = 1324.94 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.28 mm^{-1}
T = 293 K
0.25 × 0.18 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.934, T_{max} = 0.957
12868 measured reflections
3032 independent reflections
2693 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.103
S = 1.05
3032 reflections
197 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5···O1w	0.85 (1)	1.71 (1)	2.552 (2)	171 (2)
O6—H6···O2	0.86 (1)	1.68 (1)	2.539 (1)	177 (2)
O1w—H11···O1	0.84 (1)	1.93 (1)	2.765 (2)	170 (3)
O1w—H12···O3^{i}	0.85 (1)	1.99 (2)	2.783 (2)	157 (3)
N1—H1n···O4^{ii}	0.86	1.95	2.766 (2)	158
N2—H2n···O3^{iii}	0.86	1.87	2.705 (2)	163

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalClear* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2675).

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supplementary materials

Acta Cryst. (2009). E**65**, o3146 [**doi:10.1107/S1600536809048521**]

Bis(4-hydroxypyridinium) sulfate monohydrate

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Experimental

Copper nitrate (0.37 g, 2 mmol) and 4-hydroxypyridine-3-sulfonic acid (0.35 g, 2 mmol) were dissolved in hot water. The pH value was adjusted to 6 with 0.1 *M* sodium hydroxide. The solution was allowed to evaporate slowly at room temperature; colorless prismatic crystals were isolated from the blue-green solution after several days.

Refinement

Carbon-bound H-atoms were placed in calculated positions (C–H 0.93 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2U(C). The water H-atoms were located in a difference Fourier map, and were refined with a distance restraint of O–H = 0.85±0.01 Å; their temperature factors were refined. The pyridinium H-atoms could be found in a difference Fourier map; however, their refinement led to somewhat unsatisfactory angles. As such, their positions were fixed and their temperatures tied to those of the parent atoms.

Figures

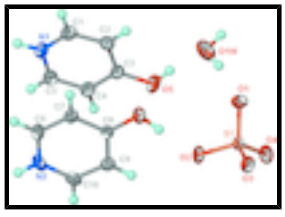

Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of $2[C_5H_6NO][SO_4]\cdot H_2O$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

Bis(4-hydroxypyridinium) sulfate monohydrate

Crystal data

$2C_5H_6NO^+\cdot SO_4^{2-}\cdot H_2O$	F_{000} = 640
M_r = 306.29	D_x = 1.535 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 11052 reflections
a = 7.1404 (2) Å	θ = 3.0–27.4°
b = 19.9797 (5) Å	μ = 0.28 mm^{-1}
c = 9.5148 (2) Å	T = 293 K
β = 102.557 (1)°	Prism, colorless
V = 1324.94 (6) Å^3	0.25 × 0.18 × 0.16 mm
Z = 4	

Data collection

Rigaku R-AXIS RAPID IP diffractometer	3032 independent reflections
Radiation source: fine-focus sealed tube	2693 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.020$
$T = 293$ K	$\theta_{max} = 27.4^{o}$
ω scan	$\theta_{min} = 3.0^{o}$
Absorption correction: Multi-scan (ABSCOR; Higashi, 1995)	$h = -9 \rightarrow 9$
$T_{min} = 0.934$, $T_{max} = 0.957$	$k = -25 \rightarrow 25$
12868 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.103$	$w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 0.2237P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
3032 reflections	$\Delta\rho_{max} = 0.42$ e Å^{-3}
197 parameters	$\Delta\rho_{min} = -0.43$ e Å^{-3}
6 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.61983 (4)	0.073598 (14)	0.24878 (3)	0.02657 (12)
O1	0.43221 (15)	0.06385 (5)	0.15168 (11)	0.0397 (3)
O2	0.64861 (17)	0.14531 (5)	0.28579 (12)	0.0436 (3)
O3	0.77259 (15)	0.05185 (5)	0.17503 (12)	0.0388 (2)
O4	0.63392 (17)	0.03440 (5)	0.38109 (10)	0.0417 (3)
O5	0.20084 (17)	0.22956 (5)	0.36294 (12)	0.0425 (3)
O6	0.47857 (16)	0.23613 (5)	0.11899 (11)	0.0373 (2)
O1W	0.1093 (2)	0.12590 (7)	0.2064 (2)	0.0645 (4)
N1	0.04132 (18)	0.41179 (6)	0.18890 (13)	0.0356 (3)
H1N	0.0088	0.4507	0.1532	0.043*
N2	0.62608 (18)	0.42205 (6)	0.27653 (15)	0.0379 (3)
H2N	0.6556	0.4617	0.3091	0.045*
C1	−0.0033 (2)	0.35736 (7)	0.10572 (15)	0.0355 (3)
H1	−0.0686	0.3623	0.0105	0.043*
C2	0.0458 (2)	0.29479 (7)	0.15884 (14)	0.0321 (3)

H2	0.0135	0.2573	0.1006	0.039*
C3	0.14570 (19)	0.28776 (7)	0.30255 (14)	0.0304 (3)
C4	0.1913 (2)	0.34564 (7)	0.38645 (14)	0.0340 (3)
H4	0.2585	0.3424	0.4816	0.041*
C5	0.1361 (2)	0.40666 (7)	0.32736 (16)	0.0358 (3)
H5A	0.1643	0.4451	0.3831	0.043*
C6	0.5135 (2)	0.41430 (7)	0.14439 (17)	0.0382 (3)
H6A	0.4688	0.4519	0.0897	0.046*
C7	0.4642 (2)	0.35222 (7)	0.08949 (14)	0.0329 (3)
H7	0.3870	0.3474	−0.0022	0.039*
C8	0.53127 (18)	0.29565 (6)	0.17300 (13)	0.0271 (3)
C9	0.64828 (19)	0.30528 (7)	0.31067 (14)	0.0304 (3)
H9	0.6946	0.2688	0.3685	0.036*
C10	0.6930 (2)	0.36886 (8)	0.35840 (15)	0.0350 (3)
H10	0.7712	0.3755	0.4491	0.042*
H5	0.158 (3)	0.1970 (8)	0.308 (2)	0.060 (6)*
H6	0.540 (3)	0.2060 (8)	0.1754 (18)	0.053 (5)*
H11	0.204 (3)	0.1028 (11)	0.195 (3)	0.076 (7)*
H12	0.021 (3)	0.1002 (12)	0.221 (3)	0.093 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.03062 (19)	0.01762 (17)	0.02844 (18)	0.00117 (10)	−0.00024 (13)	−0.00033 (10)
O1	0.0326 (5)	0.0376 (5)	0.0431 (6)	0.0009 (4)	−0.0045 (4)	−0.0053 (4)
O2	0.0599 (7)	0.0181 (5)	0.0440 (6)	0.0024 (4)	−0.0081 (5)	−0.0031 (4)
O3	0.0371 (5)	0.0294 (5)	0.0513 (6)	0.0046 (4)	0.0123 (5)	0.0042 (4)
O4	0.0610 (7)	0.0301 (5)	0.0308 (5)	−0.0052 (5)	0.0030 (4)	0.0034 (4)
O5	0.0543 (7)	0.0295 (5)	0.0406 (6)	0.0081 (5)	0.0032 (5)	0.0031 (4)
O6	0.0479 (6)	0.0239 (5)	0.0354 (5)	−0.0011 (4)	−0.0010 (4)	−0.0020 (4)
O1W	0.0465 (7)	0.0422 (7)	0.1120 (11)	−0.0086 (6)	0.0328 (8)	−0.0245 (7)
N1	0.0367 (6)	0.0292 (6)	0.0408 (6)	0.0047 (5)	0.0086 (5)	0.0058 (5)
N2	0.0384 (7)	0.0271 (6)	0.0497 (7)	−0.0089 (5)	0.0132 (5)	−0.0081 (5)
C1	0.0324 (7)	0.0414 (8)	0.0317 (6)	0.0018 (6)	0.0045 (5)	0.0033 (5)
C2	0.0316 (7)	0.0323 (6)	0.0319 (6)	−0.0015 (5)	0.0056 (5)	−0.0045 (5)
C3	0.0282 (6)	0.0295 (6)	0.0341 (6)	0.0034 (5)	0.0085 (5)	0.0016 (5)
C4	0.0347 (7)	0.0348 (7)	0.0309 (6)	0.0027 (5)	0.0034 (5)	−0.0028 (5)
C5	0.0369 (7)	0.0305 (6)	0.0396 (7)	0.0012 (6)	0.0077 (6)	−0.0039 (6)
C6	0.0403 (8)	0.0264 (6)	0.0481 (8)	0.0004 (6)	0.0099 (6)	0.0078 (6)
C7	0.0333 (7)	0.0308 (6)	0.0321 (6)	0.0001 (5)	0.0017 (5)	0.0050 (5)
C8	0.0257 (6)	0.0246 (6)	0.0309 (6)	−0.0005 (4)	0.0060 (5)	0.0000 (5)
C9	0.0285 (6)	0.0323 (6)	0.0294 (6)	0.0011 (5)	0.0042 (5)	0.0022 (5)
C10	0.0288 (6)	0.0408 (7)	0.0350 (7)	−0.0065 (5)	0.0055 (5)	−0.0072 (6)

Geometric parameters (Å, °)

S1—O4	1.4674 (10)	C1—C2	1.365 (2)
S1—O1	1.4656 (10)	C1—H1	0.9300
S1—O2	1.4790 (10)	C2—C3	1.4051 (18)

S1—O3	1.4845 (10)	C2—H2	0.9300
O5—C3	1.3187 (16)	C3—C4	1.4026 (19)
O5—H5	0.849 (9)	C4—C5	1.364 (2)
O6—C8	1.3175 (15)	C4—H4	0.9300
O6—H6	0.861 (9)	C5—H5A	0.9300
O1W—H11	0.844 (10)	C6—C7	1.362 (2)
O1W—H12	0.847 (10)	C6—H6A	0.9300
N1—C1	1.3419 (19)	C7—C8	1.4046 (18)
N1—C5	1.3479 (19)	C7—H7	0.9300
N1—H1N	0.8600	C8—C9	1.4054 (18)
N2—C10	1.343 (2)	C9—C10	1.3633 (19)
N2—C6	1.346 (2)	C9—H9	0.9300
N2—H2N	0.8600	C10—H10	0.9300
O4—S1—O1	110.65 (7)	C4—C3—C2	118.51 (12)
O4—S1—O2	109.43 (6)	C5—C4—C3	119.46 (12)
O1—S1—O2	109.85 (6)	C5—C4—H4	120.3
O4—S1—O3	109.21 (6)	C3—C4—H4	120.3
O1—S1—O3	109.15 (6)	N1—C5—C4	120.62 (13)
O2—S1—O3	108.53 (7)	N1—C5—H5A	119.7
C3—O5—H5	112.0 (15)	C4—C5—H5A	119.7
C8—O6—H6	109.0 (14)	N2—C6—C7	121.01 (13)
H11—O1W—H12	109 (3)	N2—C6—H6A	119.5
C1—N1—C5	121.28 (12)	C7—C6—H6A	119.5
C1—N1—H1N	119.4	C6—C7—C8	119.20 (13)
C5—N1—H1N	119.4	C6—C7—H7	120.4
C10—N2—C6	121.06 (12)	C8—C7—H7	120.4
C10—N2—H2N	119.5	O6—C8—C7	118.19 (12)
C6—N2—H2N	119.5	O6—C8—C9	123.28 (11)
N1—C1—C2	120.98 (13)	C7—C8—C9	118.52 (12)
N1—C1—H1	119.5	C10—C9—C8	119.13 (12)
C2—C1—H1	119.5	C10—C9—H9	120.4
C1—C2—C3	119.14 (12)	C8—C9—H9	120.4
C1—C2—H2	120.4	N2—C10—C9	121.07 (12)
C3—C2—H2	120.4	N2—C10—H10	119.5
O5—C3—C4	117.95 (12)	C9—C10—H10	119.5
O5—C3—C2	123.54 (12)		
C5—N1—C1—C2	0.1 (2)	C10—N2—C6—C7	−0.1 (2)
N1—C1—C2—C3	−0.5 (2)	N2—C6—C7—C8	0.4 (2)
C1—C2—C3—O5	−179.30 (13)	C6—C7—C8—O6	178.62 (13)
C1—C2—C3—C4	0.1 (2)	C6—C7—C8—C9	−0.3 (2)
O5—C3—C4—C5	−179.92 (13)	O6—C8—C9—C10	−179.00 (12)
C2—C3—C4—C5	0.7 (2)	C7—C8—C9—C10	−0.1 (2)
C1—N1—C5—C4	0.7 (2)	C6—N2—C10—C9	−0.4 (2)
C3—C4—C5—N1	−1.1 (2)	C8—C9—C10—N2	0.5 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O1w	0.85 (1)	1.71 (1)	2.552 (2)	171 (2)

O6—H6···O2	0.86 (1)	1.68 (1)	2.539 (1)	177 (2)
O1w—H11···O1	0.84 (1)	1.93 (1)	2.765 (2)	170 (3)
O1w—H12···O3^{i}	0.85 (1)	1.99 (2)	2.783 (2)	157 (3)
N1—H1n···O4^{ii}	0.86	1.95	2.766 (2)	158
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Fig. 1