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4-Aminopyridinium-3-sulfonate monohydrate

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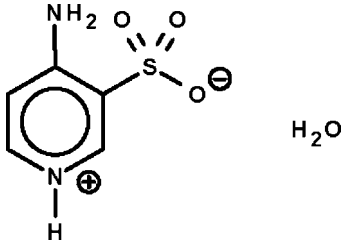
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.044; wR factor = 0.137; data-to-parameter ratio = 12.1.

The reaction of 4-aminopyridine and oleum yielded the title hydrated zwitterion, $C_5H_6N_2O_3S\cdot H_2O$. There are two formula units in the asymmetric unit. The H and non-H atoms of both zwitterions lie on a mirror plane except for one sulfonate O atom. The water molecules are also situated on a mirror plane. In the crystal, the zwitterions and water molecules are linked by O—H···O and N—H···O hydrogen bonds, generating a three-dimensional network.

Related literature

The analogous reaction of 4-hydroxypyridine with oleum yielded hydronium 4-oxo-1,4-dihydropyridine-3-sulfonate dihydrate and 4-hydroxypyridinium-3-sulfonate; see: Zhu *et al.* (2009, 2011).



Experimental

Crystal data

$C_5H_6N_2O_3S\cdot H_2O$
M_r = 192.19
Orthorhombic, *Pnma*
a = 31.6739 (13) Å
b = 6.5824 (3) Å
c = 7.3204 (3) Å
V = 1526.23 (11) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 293 K
0.21 × 0.19 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.921, T_{max} = 0.939
22965 measured reflections
1898 independent reflections
1325 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.137
S = 1.17
1898 reflections
157 parameters
8 restraints
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1w^{i}	0.88 (2)	1.99 (2)	2.820 (4)	158 (3)
N2—H22···O2^{ii}	0.88 (2)	2.01 (2)	2.886 (3)	172 (3)
N3—H3···O1w^{iii}	0.88 (2)	2.15 (3)	2.871 (4)	139 (3)
N4—H42···O4^{iv}	0.88 (2)	1.99 (2)	2.869 (3)	173 (4)
O1w—H1w···O1	0.84 (2)	1.99 (2)	2.826 (3)	173 (3)
O2w—H2w···O3	0.85 (2)	2.02 (2)	2.864 (2)	171 (3)

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (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, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2250).

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Acta Cryst. (2011). E**67**, o456 [doi:10.1107/S1600536811002145]

4-Aminopyridinium-3-sulfonate monohydrate

Zhi-Biao Zhu, Shan Gao and Seik Weng Ng

S1. Comment

A previous reaction of 4-hydroxpyridine and oleum gave the salt, hydronium 4-oxo-1,4-dihydropyridine-3-sulfonate dihydrate (Zhu *et al.*, 2009); a later repeat of the synthesis gave zwitterionic 4-hydroxypyridinium-3-sulfonate (Zhu *et al.*, 2011). The studies were extended to 4-aminopyridine which upon reaction with oleum gave zwitterionic 4-amino-pyridinium-3-sulfonate as a monohydrate (Scheme I, Fig. 1). The bonds in the ring are delocalized bonds. Adjacent zwitterions and water molecues are linked by N–H···O and O–H···O hydrogen bonds into a three-dimensional network (Tablel 1).

S2. Experimental

4-Aminopyridine (10 mmol) was dissolved in 20% oleum (10 ml). The solution was heated to 393 K for 4 days. After it was cooled, the excess oleum was decanted. Recrystallization of the solid from water gave colorless crystals.

S3. Refinement

Hydrogen 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_{eq}(C). The amino and water H atoms were located in a difference Fourier map, and were refined with distance restraints of O–H 0.84±0.01 Å and N–H 0.88±0.01 Å; their temperature factors were tied by a factor of 1.2–1.5U_{eq}(N,O).

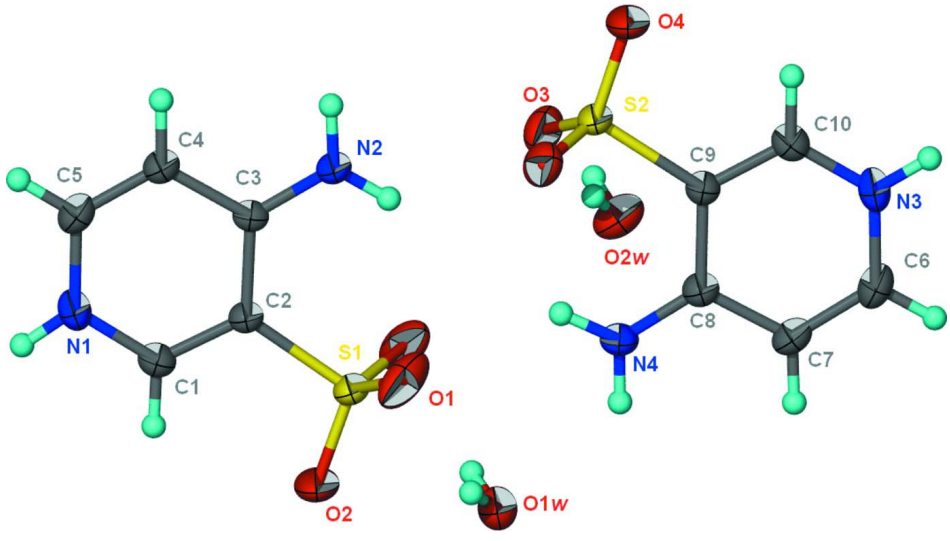

Figure 1

Thermal ellipsoid plot (Barbour, 2001) of the two independent molecules of $C_5H_6N_2O_3S{\cdot}H_2O$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

4-Aminopyridinium-3-sulfonate monohydrate

Crystal data

$C_5H_6N_2O_3S·H_2O$
M_r = 192.19
Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
a = 31.6739 (13) Å
b = 6.5824 (3) Å
c = 7.3204 (3) Å
V = 1526.23 (11) Å^3
Z = 8
$F(000)$ = 800
D_x = 1.673 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 13913 reflections
θ = 3.1–27.5°
μ = 0.40 mm^{-1}
T = 293 K
Prism, colorless
0.21 × 0.19 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.921, T_{max} = 0.939
22965 measured reflections
1898 independent reflections
1325 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 27.5°, θ_{min} = 3.1°
h = −41→41
k = −8→8
l = −9→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.137
S = 1.17
1898 reflections
157 parameters
8 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}
S1	0.55812 (2)	0.2500	0.86929 (9)	0.0348 (3)
S2	0.66689 (2)	0.2500	0.36003 (10)	0.0360 (3)
O1	0.58140 (6)	0.4293 (3)	0.8206 (3)	0.0647 (6)
O2	0.54212 (8)	0.2500	1.0518 (3)	0.0712 (10)
O1W	0.62156 (8)	0.7500	1.0095 (3)	0.0451 (6)
H1W	0.6107 (9)	0.648 (4)	0.959 (4)	0.068*
O2W	0.67561 (10)	−0.2500	0.6401 (4)	0.0573 (8)
H2W	0.6649 (10)	−0.151 (4)	0.582 (4)	0.086*
O3	0.64409 (5)	0.0686 (3)	0.4112 (2)	0.0496 (5)
O4	0.68205 (8)	0.2500	0.1750 (3)	0.0570 (8)
N1	0.43845 (8)	0.2500	0.7058 (4)	0.0413 (7)
H1	0.4151 (7)	0.2500	0.770 (4)	0.050*
N2	0.55273 (8)	0.2500	0.4434 (3)	0.0366 (7)

H21	0.5763 (6)	0.2500	0.505 (4)	0.044*
H22	0.5522 (11)	0.2500	0.3234 (14)	0.044*
N3	0.78781 (8)	0.2500	0.5065 (4)	0.0416 (7)
H3	0.8121 (6)	0.2500	0.449 (4)	0.050*
N4	0.67536 (8)	0.2500	0.7841 (4)	0.0443 (8)
H41	0.6504 (6)	0.2500	0.731 (5)	0.053*
H42	0.6752 (12)	0.2500	0.9046 (15)	0.053*
C1	0.47379 (9)	0.2500	0.8053 (4)	0.0367 (8)
H1A	0.4717	0.2500	0.9320	0.044*
C2	0.51300 (9)	0.2500	0.7265 (4)	0.0296 (7)
C3	0.51604 (9)	0.2500	0.5320 (4)	0.0285 (7)
C4	0.47767 (9)	0.2500	0.4337 (4)	0.0330 (7)
H4	0.4783	0.2500	0.3067	0.040*
C5	0.44023 (11)	0.2500	0.5209 (4)	0.0408 (8)
H5	0.4153	0.2500	0.4535	0.049*
C6	0.78747 (10)	0.2500	0.6914 (5)	0.0449 (9)
H6	0.8129	0.2500	0.7549	0.054*
C7	0.75061 (10)	0.2500	0.7851 (4)	0.0399 (8)
H7	0.7510	0.2500	0.9121	0.048*
C8	0.71128 (9)	0.2500	0.6911 (4)	0.0344 (7)
C9	0.71321 (10)	0.2500	0.4964 (4)	0.0332 (7)
C10	0.75175 (10)	0.2500	0.4121 (4)	0.0368 (8)
H10	0.7529	0.2500	0.2852	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0304 (4)	0.0518 (6)	0.0223 (4)	0.000	−0.0034 (3)	0.000
S2	0.0287 (4)	0.0574 (6)	0.0219 (4)	0.000	−0.0017 (3)	0.000
O1	0.0602 (11)	0.0694 (15)	0.0644 (12)	−0.0289 (10)	−0.0289 (10)	0.0189 (10)
O2	0.0466 (15)	0.144 (3)	0.0225 (12)	0.000	−0.0016 (11)	0.000
O1W	0.0354 (13)	0.0573 (18)	0.0428 (14)	0.000	0.0008 (10)	0.000
O2W	0.0606 (18)	0.065 (2)	0.0457 (16)	0.000	−0.0179 (12)	0.000
O3	0.0365 (9)	0.0631 (13)	0.0493 (10)	−0.0121 (9)	−0.0081 (7)	0.0079 (9)
O4	0.0438 (14)	0.104 (2)	0.0237 (11)	0.000	−0.0003 (10)	0.000
N1	0.0255 (13)	0.059 (2)	0.0388 (15)	0.000	0.0049 (11)	0.000
N2	0.0287 (13)	0.0584 (19)	0.0227 (12)	0.000	−0.0021 (11)	0.000
N3	0.0240 (13)	0.055 (2)	0.0452 (16)	0.000	0.0040 (11)	0.000
N4	0.0337 (15)	0.076 (2)	0.0228 (13)	0.000	0.0004 (11)	0.000
C1	0.0335 (16)	0.050 (2)	0.0265 (14)	0.000	0.0026 (13)	0.000
C2	0.0280 (14)	0.0379 (19)	0.0227 (14)	0.000	−0.0013 (11)	0.000
C3	0.0303 (15)	0.0324 (18)	0.0227 (13)	0.000	0.0013 (11)	0.000
C4	0.0311 (15)	0.041 (2)	0.0267 (14)	0.000	−0.0032 (12)	0.000
C5	0.0325 (16)	0.054 (2)	0.0363 (17)	0.000	−0.0078 (13)	0.000
C6	0.0307 (16)	0.058 (2)	0.0461 (18)	0.000	−0.0103 (15)	0.000
C7	0.0372 (17)	0.052 (2)	0.0304 (16)	0.000	−0.0086 (14)	0.000
C8	0.0314 (16)	0.045 (2)	0.0270 (14)	0.000	−0.0013 (12)	0.000
C9	0.0279 (15)	0.046 (2)	0.0261 (14)	0.000	0.0004 (11)	0.000

C10	0.0333 (16)	0.045 (2)	0.0322 (16)	0.000	0.0038 (13)	0.000

Geometric parameters (Å, º)

S1—O2	1.429 (2)	N3—H3	0.88 (2)
S1—O1	1.436 (2)	N4—C8	1.326 (4)
S1—O1^{i}	1.436 (2)	N4—H41	0.88 (2)
S1—C2	1.771 (3)	N4—H42	0.88 (2
S2—O4	1.437 (2)	C1—C2	1.369 (4)
S2—O3	1.4451 (18)	C1—H1A	0.9300
S2—O3^{i}	1.4451 (18)	C2—C3	1.427 (4)
S2—C9	1.775 (3)	C3—C4	1.412 (4)
O1W—H1W	0.84 (3)	C4—C5	1.347 (4)
O2W—H2W	0.85 (2)	C4—H4	0.9300
N1—C1	1.335 (4)	C5—H5	0.9300
N1—C5	1.355 (4)	C6—C7	1.354 (5)
N1—H1	0.878 (10)	C6—H6	0.9300
N2—C3	1.331 (4)	C7—C8	1.423 (4)
N2—H21	0.87 (2)	C7—H7	0.9300
N2—H22	0.88 (2)	C8—C9	1.427 (4)
N3—C10	1.335 (4)	C9—C10	1.368 (4)
N3—C6	1.354 (4)	C10—H10	0.9300
O2—S1—O1	114.46 (10)	C1—C2—C3	118.8 (3)
O2—S1—O1^{i}	114.46 (10)	C1—C2—S1	118.9 (2)
O1—S1—O1^{i}	110.5 (2)	C3—C2—S1	122.3 (2)
O2—S1—C2	105.40 (14)	N2—C3—C4	120.2 (2)
O1—S1—C2	105.54 (9)	N2—C3—C2	123.0 (3)
O1^{i}—S1—C2	105.54 (9)	C4—C3—C2	116.8 (3)
O4—S2—O3	114.29 (9)	C5—C4—C3	121.1 (3)
O4—S2—O3^{i}	114.29 (9)	C5—C4—H4	119.5
O3—S2—O3^{i}	111.47 (16)	C3—C4—H4	119.5
O4—S2—C9	104.71 (14)	C4—C5—N1	120.7 (3)
O3—S2—C9	105.51 (8)	C4—C5—H5	119.7
O3^{i}—S2—C9	105.51 (8)	N1—C5—H5	119.7
C1—N1—C5	120.7 (3)	N3—C6—C7	120.9 (3)
C1—N1—H1	114 (2)	N3—C6—H6	119.6
C5—N1—H1	125 (2)	C7—C6—H6	119.6
C3—N2—H21	120 (2)	C6—C7—C8	120.7 (3)
C3—N2—H22	118 (2)	C6—C7—H7	119.7
H21—N2—H22	122 (3)	C8—C7—H7	119.7
C10—N3—C6	120.7 (3)	N4—C8—C7	120.2 (3)
C10—N3—H3	120 (2)	N4—C8—C9	123.4 (3)
C6—N3—H3	119 (2)	C7—C8—C9	116.4 (3)
C8—N4—H41	123 (3)	C10—C9—C8	119.3 (3)
C8—N4—H42	121 (3)	C10—C9—S2	119.0 (2)
H41—N4—H42	116 (4)	C8—C9—S2	121.8 (2)
N1—C1—C2	122.0 (3)	N3—C10—C9	122.0 (3)

N1—C1—H1A	119.0	N3—C10—H10	119.0
C2—C1—H1A	119.0	C9—C10—H10	119.0
C5—N1—C1—C2	0.0	C10—N3—C6—C7	0.0
N1—C1—C2—C3	0.0	N3—C6—C7—C8	0.0
N1—C1—C2—S1	180.0	C6—C7—C8—N4	180.0
O2—S1—C2—C1	0.0	C6—C7—C8—C9	0.0
O1—S1—C2—C1	−121.49 (11)	N4—C8—C9—C10	180.0
O1^{i}—S1—C2—C1	121.49 (11)	C7—C8—C9—C10	0.0
O2—S1—C2—C3	180.0	N4—C8—C9—S2	0.0
O1—S1—C2—C3	58.51 (11)	C7—C8—C9—S2	180.0
O1^{i}—S1—C2—C3	−58.51 (11)	O4—S2—C9—C10	0.0
C1—C2—C3—N2	180.0	O3—S2—C9—C10	120.95 (9)
S1—C2—C3—N2	0.0	O3^{i}—S2—C9—C10	−120.95 (9)
C1—C2—C3—C4	0.0	O4—S2—C9—C8	180.0
S1—C2—C3—C4	180.0	O3—S2—C9—C8	−59.05 (9)
N2—C3—C4—C5	180.0	O3^{i}—S2—C9—C8	59.05 (9)
C2—C3—C4—C5	0.0	C6—N3—C10—C9	0.0
C3—C4—C5—N1	0.0	C8—C9—C10—N3	0.0
C1—N1—C5—C4	0.0	S2—C9—C10—N3	180.0

Symmetry code: (i) x, $-y+1/2$, z.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1w^{ii}	0.88 (2)	1.99 (2)	2.820 (4)	158 (3)
N2—H22···O2^{iii}	0.88 (2)	2.01 (2)	2.886 (3)	172 (3)
N3—H3···O1w^{iv}	0.88 (2)	2.15 (3)	2.871 (4)	139 (3)
N4—H42···O4^{v}	0.88 (2)	1.99 (2)	2.869 (3)	173 (4)
O1w—H1w···O1	0.84 (2)	1.99 (2)	2.826 (3)	173 (3)
O2w—H2w···O3	0.85 (2)	2.02 (2)	2.864 (2)	171 (3)

Symmetry codes: (ii) $-x+1$, $-y+1$, $-z+2$; (iii) x, y, $z-1$; (iv) $-x+3/2$, $-y+1$, $z-1/2$; (v) x, y, $z+1$.