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Hydronium 4-oxo-1,4-dihydropyridine-3-sulfonate dihydrate

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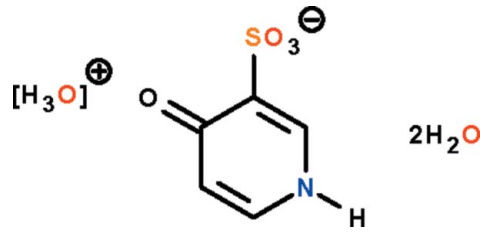
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.049; wR factor = 0.170; data-to-parameter ratio = 14.7.

2-Hydroxypyridine when treated with concentrated sulfuric acid is sulfonated at the 3-position to yield the title hydrated salt, $H_3O^+\cdot C_5H_4NO_3S^-\cdot 2H_2O$. In the crystal structure, the cations, anions and uncoordinated water molecules are linked by extensive O—H···O and N—H···O hydrogen bonds into a three-dimensional network. The crystal studied is a non-merohedral twin with a twin component of 36%.

Related literature

For the treatment of non-merohedral twins, see: Spek (2003). For the cobalt salt of the anion, see: Zhu *et al.* (2007).



Experimental

Crystal data

$H_3O^+\cdot C_5H_4NO_4S^-\cdot 2H_2O$
M_r = 229.21
Triclinic, $P\overline{1}$
a = 6.6610 (8) Å
b = 7.4179 (10) Å
c = 10.0514 (11) Å
α = 90.922 (4)°
β = 94.543 (3)°
γ = 96.226 (4)°
V = 492.01 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.34 mm^{-1}
T = 293 K
0.25 × 0.22 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.856, T_{max} = 0.932
4711 measured reflections
2234 independent reflections
1719 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.170
S = 1.06
2234 reflections
152 parameters
13 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1w—H11···O1	0.85 (1)	1.90 (1)	2.745 (4)	175 (5)
O1w—H12···O2^{i}	0.85 (1)	2.50 (4)	2.983 (4)	116 (3)
O2w—H21···O1w	0.85 (1)	1.89 (1)	2.741 (4)	175 (6)
O2w—H22···O4^{ii}	0.85 (1)	2.07 (2)	2.910 (4)	168 (6)
O3w—H31···O2^{i}	0.86 (1)	2.12 (2)	2.951 (4)	165 (5)
O3w—H32···O2^{ii}	0.85 (1)	2.07 (2)	2.898 (4)	162 (5)
O3w—H33···O3^{iii}	0.85 (1)	2.18 (2)	2.936 (4)	147 (4)
N1—H1···O3^{iv}	0.86 (1)	2.05 (2)	2.857 (4)	156 (5)

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

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: XU2628).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalClear*. Rigaku/MSC Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Westrip, S. P. (2009). *publCIF*. In preparation.
Zhu, Z.-B., Gao, S., Huo, L.-H. & Zhao, H. (2007). *Acta Cryst.* E**63**, m3126–m3127.

supplementary materials

Acta Cryst. (2009). E**65**, o2687 [**doi:10.1107/S1600536809040641**]

Hydronium 4-oxo-1,4-dihydropyridine-3-sulfonate dihydrate

Z.-B. Zhu, S. Gao and S. W. Ng

Experimental

A 1:3 molar mixture of 4-hydroxypyridine and oleum (20%) was heated at 483 K for 3 h. Barium carbonate was added to the cool mixture until no more carbon dioxide evolved. Colorless crystals were isolated from the filtered solution after several days. CH&N elemental analysis. Calc. for $C_5H_{10}NO_7S$: C 26.20, H 4.84, N 6.11%; found: C 26.36, H 4.48, N 6.11%.

Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.93 to 0.97 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2U(C). The water, oxonium and amino H-atoms were located in a difference Fourier map and refined with a distance restraint of O–H = N–H 0.85±0.01 Å. The temperature factors of some of the atoms could not be refined; as such, all temperature factors were tied.

The crystal is a non-merohedral twin as shown by *PLATON* (Spek, 2003).

Figures

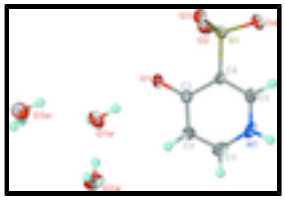

Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of $[H_3O][C_5H_4NO_3S]\cdot 2H_2O$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

Hydronium 4-oxo-1,4-dihydropyridine-3-sulfonate dihydrate

Crystal data

$H_3O^+\cdot C_5H_4NO_4S^-\cdot 2H_2O$	$Z = 2$
$M_r = 229.21$	$F_{000} = 240$
Triclinic, $P\overline{1}$	$D_x = 1.547$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, λ = 0.71073 Å
$a = 6.6610$ (8) Å	Cell parameters from 3881 reflections
$b = 7.4179$ (10) Å	θ = 3.1–27.5°
$c = 10.0514$ (11) Å	μ = 0.34 mm^{-1}
α = 90.922 (4)°	$T = 293$ K
β = 94.543 (3)°	Block, colorless
γ = 96.226 (4)°	0.25 × 0.22 × 0.20 mm
$V = 492.01$ (10) Å^3	

Data collection

Rigaku R-AXIS RAPID IP diffractometer	2234 independent reflections
Radiation source: fine-focus sealed tube	1719 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.022$
$T = 293$ K	$\theta_{max} = 27.5^o$
ω scans	$\theta_{min} = 3.1^o$
Absorption correction: Multi-scan (ABSCOR; Higashi, 1995)	$h = -8 \rightarrow 8$
$T_{min} = 0.856$, $T_{max} = 0.932$	$k = -9 \rightarrow 9$
4711 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.170$	$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2 + 0.6366P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
2234 reflections	$\Delta\rho_{max} = 0.65$ e Å^{-3}
152 parameters	$\Delta\rho_{min} = -0.59$ e Å^{-3}
13 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.68686 (13)	0.38798 (11)	0.16672 (8)	0.0280 (2)
O1	0.6502 (4)	0.2383 (4)	0.4423 (2)	0.0363 (6)
O2	0.5597 (4)	0.2165 (3)	0.1408 (2)	0.0365 (6)
O3	0.5787 (4)	0.5226 (3)	0.2300 (2)	0.0350 (6)
O4	0.7845 (4)	0.4562 (4)	0.0509 (2)	0.0402 (6)
O1W	0.5750 (5)	0.0846 (4)	0.6825 (3)	0.0479 (7)
H11	0.605 (9)	0.135 (5)	0.610 (3)	0.072*
H12	0.523 (8)	−0.024 (3)	0.664 (4)	0.072*

O2W	0.8700 (5)	0.1491 (5)	0.8890 (3)	0.0582 (8)
H21	0.783 (7)	0.132 (7)	0.822 (4)	0.087*
H22	0.855 (9)	0.249 (5)	0.928 (5)	0.087*
O3W	0.2908 (5)	0.1387 (4)	0.9010 (3)	0.0540 (8)
H31	0.310 (8)	0.028 (2)	0.887 (4)	0.081*
H32	0.350 (7)	0.176 (5)	0.976 (2)	0.081*
H33	0.338 (7)	0.204 (5)	0.839 (3)	0.081*
N1	1.2314 (5)	0.3608 (5)	0.3510 (3)	0.0403 (7)
H1	1.351 (3)	0.385 (7)	0.327 (5)	0.060*
C1	1.1944 (6)	0.2958 (6)	0.4722 (4)	0.0405 (9)
H1A	1.3022	0.2809	0.5342	0.049*
C2	1.0013 (5)	0.2520 (5)	0.5047 (4)	0.0346 (8)
H2	0.9795	0.2068	0.5887	0.042*
C3	0.8321 (5)	0.2734 (4)	0.4136 (3)	0.0278 (6)
C4	0.8828 (5)	0.3435 (4)	0.2858 (3)	0.0264 (7)
C5	1.0802 (6)	0.3834 (5)	0.2586 (4)	0.0334 (7)
H5	1.1100	0.4267	0.1752	0.040*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0305 (4)	0.0281 (4)	0.0249 (4)	0.0000 (3)	0.0025 (3)	0.0033 (3)
O1	0.0272 (12)	0.0504 (15)	0.0308 (12)	−0.0019 (11)	0.0066 (10)	0.0093 (11)
O2	0.0385 (13)	0.0313 (13)	0.0367 (13)	−0.0032 (11)	−0.0062 (11)	0.0012 (10)
O3	0.0367 (13)	0.0310 (12)	0.0389 (13)	0.0080 (11)	0.0072 (11)	0.0049 (10)
O4	0.0465 (16)	0.0461 (15)	0.0281 (12)	−0.0003 (13)	0.0082 (11)	0.0093 (11)
O1W	0.0621 (19)	0.0438 (16)	0.0346 (14)	−0.0083 (15)	0.0032 (14)	0.0057 (11)
O2W	0.0456 (17)	0.066 (2)	0.062 (2)	0.0103 (17)	−0.0055 (16)	−0.0101 (16)
O3W	0.063 (2)	0.0457 (17)	0.0525 (18)	0.0037 (15)	0.0025 (16)	0.0059 (13)
N1	0.0244 (14)	0.0515 (19)	0.0452 (18)	0.0016 (14)	0.0100 (14)	−0.0040 (14)
C1	0.0287 (18)	0.050 (2)	0.043 (2)	0.0081 (16)	−0.0009 (16)	−0.0059 (17)
C2	0.0309 (18)	0.043 (2)	0.0300 (16)	0.0057 (15)	0.0013 (14)	0.0019 (14)
C3	0.0269 (15)	0.0281 (15)	0.0274 (15)	−0.0018 (13)	0.0031 (13)	0.0003 (12)
C4	0.0233 (14)	0.0282 (16)	0.0275 (15)	0.0017 (12)	0.0030 (12)	−0.0005 (12)
C5	0.0325 (17)	0.0332 (17)	0.0347 (17)	0.0002 (15)	0.0087 (15)	−0.0017 (13)

Geometric parameters (Å, °)

S1—O4	1.449 (2)	O3W—H33	0.854 (10)
S1—O2	1.457 (2)	N1—C5	1.341 (5)
S1—O3	1.459 (3)	N1—C1	1.348 (5)
S1—C4	1.762 (3)	N1—H1	0.855 (10)
O1—C3	1.268 (4)	C1—C2	1.358 (5)
O1W—H11	0.850 (10)	C1—H1A	0.9300
O1W—H12	0.854 (10)	C2—C3	1.419 (5)
O2W—H21	0.854 (10)	C2—H2	0.9300
O2W—H22	0.851 (10)	C3—C4	1.445 (4)
O3W—H31	0.855 (10)	C4—C5	1.367 (5)
O3W—H32	0.853 (10)	C5—H5	0.9300

O4—S1—O2	113.46 (15)	N1—C1—H1A	119.7
O4—S1—O3	112.83 (16)	C2—C1—H1A	119.7
O2—S1—O3	111.76 (16)	C1—C2—C3	121.7 (3)
O4—S1—C4	106.31 (16)	C1—C2—H2	119.2
O2—S1—C4	106.22 (15)	C3—C2—H2	119.2
O3—S1—C4	105.54 (15)	O1—C3—C2	123.1 (3)
H11—O1W—H12	108.9 (17)	O1—C3—C4	122.2 (3)
H21—O2W—H22	108.9 (17)	C2—C3—C4	114.7 (3)
H31—O3W—H32	109.7 (17)	C5—C4—C3	120.9 (3)
H31—O3W—H33	109.4 (17)	C5—C4—S1	119.7 (3)
H32—O3W—H33	109.9 (17)	C3—C4—S1	119.3 (2)
C5—N1—C1	121.5 (3)	N1—C5—C4	120.5 (3)
C5—N1—H1	116 (3)	N1—C5—H5	119.7
C1—N1—H1	122 (3)	C4—C5—H5	119.7
N1—C1—C2	120.7 (4)		
C5—N1—C1—C2	−0.4 (6)	O2—S1—C4—C5	124.1 (3)
N1—C1—C2—C3	−0.3 (6)	O3—S1—C4—C5	−117.1 (3)
C1—C2—C3—O1	−178.0 (4)	O4—S1—C4—C3	179.9 (3)
C1—C2—C3—C4	0.4 (5)	O2—S1—C4—C3	−58.9 (3)
O1—C3—C4—C5	178.7 (3)	O3—S1—C4—C3	59.8 (3)
C2—C3—C4—C5	0.3 (5)	C1—N1—C5—C4	1.0 (6)
O1—C3—C4—S1	1.8 (5)	C3—C4—C5—N1	−1.0 (5)
C2—C3—C4—S1	−176.6 (2)	S1—C4—C5—N1	175.9 (3)
O4—S1—C4—C5	2.9 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1w—H11···O1	0.85 (1)	1.90 (1)	2.745 (4)	175 (5)
O1w—H12···O2^{i}	0.85 (1)	2.50 (4)	2.983 (4)	116 (3)
O2w—H21···O1w	0.85 (1)	1.89 (1)	2.741 (4)	175 (6)
O2w—H22···O4^{ii}	0.85 (1)	2.07 (2)	2.910 (4)	168 (6)
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O3w—H32···O2^{ii}	0.85 (1)	2.07 (2)	2.898 (4)	162 (5)
O3w—H33···O3^{iii}	0.85 (1)	2.18 (2)	2.936 (4)	147 (4)
N1—H1···O3^{iv}	0.86 (1)	2.05 (2)	2.857 (4)	156 (5)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) *x*, *y*, *z*+1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*+1, *y*, *z*.

Fig. 1