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2,2′-[*p*-Phenylenebis(methylideneazanediyl)]dipyridinium bis(hydrogensulfate) dihydrate

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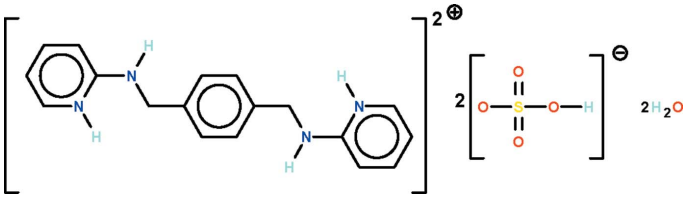
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.040; wR factor = 0.143; data-to-parameter ratio = 15.3.

The cation of the title salt, $C_{18}H_{20}N_4^{2+}\cdot 2HSO_4^-\cdot 2H_2O$, lies on a center of inversion with the mid-point directly in the middle of the *p*-phenylene ring. Within the hydrogensulfate ion, the S—O(H) bond is the longest of the S—O bonds. The dihedral angle between the central and terminal ring of the cation is 78.6 (2)°. In the crystal, the cation, anion and water molecule interact by O—H···O and N—H···O hydrogen bonds, generating a three-dimensional network.

Related literature

For the synthesis and structure of 1,4-bis(pyridine-2-aminomethyl)benzene, see: Zou *et al.* (2003).



Experimental

Crystal data

$C_{18}H_{20}N_4^{2+}\cdot 2HSO_4^-\cdot 2H_2O$
M_r = 522.55
Triclinic, $P\overline{1}$
a = 7.1718 (5) Å
b = 9.3010 (7) Å
c = 9.5113 (5) Å
α = 97.648 (2)°
β = 92.340 (2)°
γ = 114.005 (2)°
V = 571.25 (7) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 293 K
0.25 × 0.21 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.930, T_{max} = 0.949
5648 measured reflections
2583 independent reflections
1624 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.143
S = 1.14
2583 reflections
169 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1w^{i}	0.84 (1)	1.75 (1)	2.592 (4)	178 (5)
O1w—H11···O2	0.84 (1)	1.93 (2)	2.749 (3)	164 (5)
O1w—H12···O4^{ii}	0.84 (1)	1.98 (1)	2.813 (3)	174 (5)
N2—H2···O1	0.89 (1)	2.02 (2)	2.844 (3)	154 (3)
N1—H1···O4^{iii}	0.88 (1)	2.03 (1)	2.903 (3)	170 (3)

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

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: SI2312).

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supporting information

Acta Cryst. (2010). E**66**, o3300 [https://doi.org/10.1107/S1600536810047999]

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S1. Comment

The synthesis complements other reports of the coordinating ability of 1,4-bis(2-pyridylaminomethyl)benzene, a relatively flexible *N*-donor ligand having aromatic as well as aliphatic donor sites. The structure of the neutral ligand has been reported (Zou *et al.*, 2003). Protonation by a strong acid, sulfuric acid, occurs at both pyridyl nitrogen atoms to yield the hydrogensulfate salt, $C_{18}H_{20}N_4^{2+}$ $2(HSO_4)^-$·$2H_2O$ (Scheme I, Fig. 1). The cation lies on a center-of-inversion with the mid-point directly in the middle of the *p*-phenylene ring. The hydrogensulfate anion bears a hydrogen atom, so that the S–O_H bond is the longest of the S–O bonds. The cation, anion and water molecule interact by O–H···O and N–H···O hydrogen bonds to generate a three-dimensional network (Table 1).

S2. Experimental

1,4-Bis(2-pyridylaminomethyl)benzene (10 mmol, 2.90 g) was dissolved in methanol (50 ml). Strong sulfuric acid was added until the pH was 3. The solution was filtered; colorless crystals were isolated after several days.

S3. Refinement

Carbon-bound hydrogen atoms were placed in calculated positions (C–H 0.93–0.97 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2U_{eq}(C). The amino/ammonium and water H atoms were located in a difference Fourier map, and were refined with distance restraints of N–H 0.88±0.01 and O–H 0.84 + 0.01 Å; their temperature factors were refined.

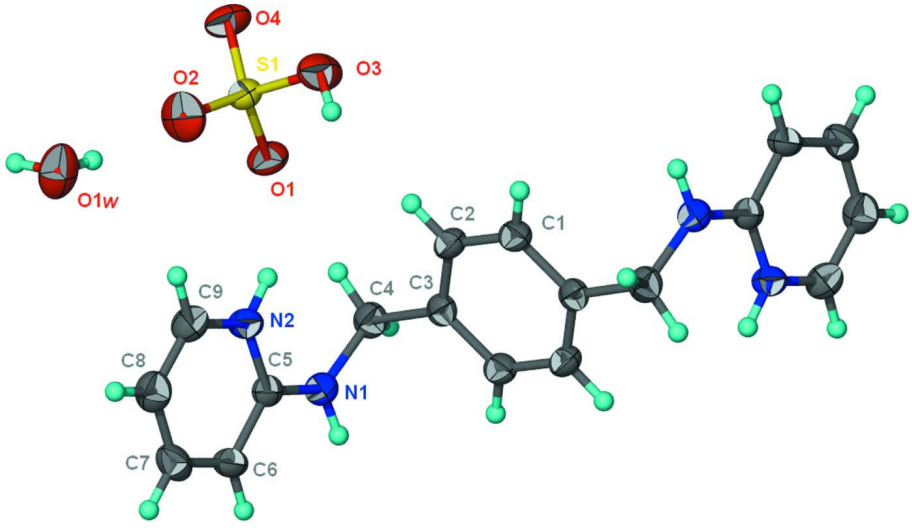

Figure 1

Thermal ellipsoid plot (Barbour, 2001) of $C_{18}H_{20}N_4^{2+}$ $2(HSO_4)^-$·$2H_2O$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The cation lies on a center-of-inversion.

2,2′-[*p*-Phenylenebis(methylideneazanediyl)]dipyridinium bis(hydrogensulfate) dihydrate

Crystal data

$C_{18}H_{20}N_4^{2+}$·$2HSO_4^-$·$2H_2O$
M_r = 522.55
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.1718 (5) Å
b = 9.3010 (7) Å
c = 9.5113 (5) Å
α = 97.648 (2)°
β = 92.340 (2)°
γ = 114.005 (2)°
V = 571.25 (7) Å^3
Z = 1
F(000) = 274
D_x = 1.519 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3948 reflections
θ = 3.1–27.4°
μ = 0.30 mm^{-1}
T = 293 K
Prism, colorless
0.25 × 0.21 × 0.18 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} = 0.930, T_{max} = 0.949
5648 measured reflections
2583 independent reflections
1624 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 27.4°, θ_{min} = 3.1°
h = −9→8
k = −12→12
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.143
S = 1.14
2583 reflections
169 parameters
5 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.3231P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.19334 (11)	0.92763 (8)	0.76081 (7)	0.0379 (2)
O1	0.1234 (3)	0.7575 (2)	0.7264 (2)	0.0508 (5)
O2	0.2506 (5)	0.9842 (3)	0.9097 (2)	0.0767 (8)
O3	0.3889 (4)	1.0040 (3)	0.6846 (3)	0.0627 (7)
H3	0.481 (5)	0.981 (5)	0.719 (4)	0.094*
O4	0.0542 (3)	0.9850 (3)	0.7002 (3)	0.0566 (6)
O1W	0.3282 (4)	1.0635 (4)	1.2016 (3)	0.0730 (8)
H11	0.286 (7)	1.023 (6)	1.1157 (19)	0.110*
H12	0.218 (4)	1.055 (6)	1.235 (5)	0.110*
N1	0.1175 (4)	0.3172 (3)	0.7485 (2)	0.0418 (6)
H1	0.112 (5)	0.220 (2)	0.740 (4)	0.063*
N2	0.2258 (4)	0.5652 (3)	0.8961 (2)	0.0388 (5)
H2	0.202 (5)	0.606 (4)	0.821 (2)	0.058*
C1	0.5953 (5)	0.6591 (3)	0.4870 (3)	0.0409 (7)
H1A	0.6588	0.7665	0.4787	0.049*
C2	0.4067 (5)	0.6003 (3)	0.5401 (3)	0.0417 (7)
H2A	0.3444	0.6687	0.5668	0.050*
C3	0.3092 (4)	0.4410 (3)	0.5541 (3)	0.0363 (6)
C4	0.1038 (5)	0.3747 (4)	0.6143 (3)	0.0432 (7)
H4A	0.0537	0.4573	0.6301	0.052*
H4B	0.0057	0.2875	0.5452	0.052*
C5	0.1854 (4)	0.4078 (3)	0.8764 (3)	0.0342 (6)
C6	0.2159 (4)	0.3435 (4)	0.9964 (3)	0.0407 (6)
H6	0.1907	0.2362	0.9874	0.049*
C7	0.2830 (5)	0.4399 (4)	1.1269 (3)	0.0492 (8)
H7	0.3020	0.3970	1.2064	0.059*
C8	0.3230 (5)	0.6011 (4)	1.1422 (3)	0.0502 (8)
H8	0.3689	0.6664	1.2308	0.060*
C9	0.2939 (4)	0.6600 (4)	1.0261 (3)	0.0453 (7)
H9	0.3206	0.7676	1.0345	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0398 (4)	0.0353 (4)	0.0421 (4)	0.0194 (3)	0.0045 (3)	0.0058 (3)
O1	0.0561 (13)	0.0329 (11)	0.0647 (14)	0.0198 (10)	0.0081 (10)	0.0079 (9)
O2	0.106 (2)	0.0816 (19)	0.0359 (13)	0.0403 (17)	−0.0082 (12)	−0.0100 (11)
O3	0.0481 (14)	0.0637 (16)	0.0861 (18)	0.0248 (12)	0.0202 (12)	0.0361 (13)
O4	0.0494 (13)	0.0527 (14)	0.0795 (16)	0.0314 (11)	0.0020 (11)	0.0175 (11)
O1W	0.0499 (15)	0.116 (2)	0.0588 (16)	0.0458 (16)	−0.0023 (12)	−0.0032 (15)

N1	0.0508 (15)	0.0357 (13)	0.0414 (13)	0.0204 (12)	0.0084 (10)	0.0059 (10)
N2	0.0420 (13)	0.0386 (14)	0.0403 (13)	0.0204 (11)	0.0020 (10)	0.0096 (10)
C1	0.0555 (18)	0.0352 (15)	0.0354 (15)	0.0226 (13)	0.0055 (12)	0.0047 (11)
C2	0.0557 (18)	0.0433 (17)	0.0371 (15)	0.0322 (15)	0.0059 (12)	0.0042 (12)
C3	0.0449 (16)	0.0423 (16)	0.0243 (13)	0.0220 (13)	0.0009 (10)	0.0025 (10)
C4	0.0469 (17)	0.0506 (18)	0.0346 (15)	0.0241 (14)	0.0008 (11)	0.0033 (12)
C5	0.0284 (13)	0.0360 (15)	0.0400 (15)	0.0138 (11)	0.0075 (10)	0.0096 (11)
C6	0.0418 (16)	0.0412 (16)	0.0472 (17)	0.0216 (13)	0.0103 (12)	0.0187 (12)
C7	0.0398 (16)	0.073 (2)	0.0443 (17)	0.0278 (15)	0.0096 (12)	0.0258 (15)
C8	0.0475 (18)	0.060 (2)	0.0428 (17)	0.0244 (16)	0.0010 (13)	0.0023 (14)
C9	0.0443 (17)	0.0401 (17)	0.0500 (17)	0.0184 (13)	0.0012 (13)	0.0009 (13)

Geometric parameters (Å, º)

S1—O2	1.425 (2)	C1—H1A	0.9300
S1—O1	1.437 (2)	C2—C3	1.385 (4)
S1—O4	1.443 (2)	C2—H2A	0.9300
S1—O3	1.551 (2)	C3—C1^{i}	1.390 (4)
O3—H3	0.84 (1)	C3—C4	1.517 (4)
O1W—H11	0.84 (1)	C4—H4A	0.9700
O1W—H12	0.84 (1)	C4—H4B	0.9700
N1—C5	1.331 (4)	C5—C6	1.406 (4)
N1—C4	1.462 (4)	C6—C7	1.371 (4)
N1—H1	0.88 (1)	C6—H6	0.9300
N2—C5	1.356 (3)	C7—C8	1.394 (5)
N2—C9	1.362 (4)	C7—H7	0.9300
N2—H2	0.89 (1)	C8—C9	1.341 (4)
C1—C2	1.382 (4)	C8—H8	0.9300
C1—C3^{i}	1.390 (4)	C9—H9	0.9300
O2—S1—O1	112.24 (15)	C1^{i}—C3—C4	119.7 (3)
O2—S1—O4	113.33 (16)	N1—C4—C3	112.3 (2)
O1—S1—O4	113.05 (14)	N1—C4—H4A	109.1
O2—S1—O3	107.05 (17)	C3—C4—H4A	109.1
O1—S1—O3	107.22 (14)	N1—C4—H4B	109.1
O4—S1—O3	103.15 (13)	C3—C4—H4B	109.1
S1—O3—H3	109 (3)	H4A—C4—H4B	107.9
H11—O1W—H12	101 (5)	N1—C5—N2	121.3 (2)
C5—N1—C4	125.7 (2)	N1—C5—C6	121.2 (3)
C5—N1—H1	117 (2)	N2—C5—C6	117.5 (2)
C4—N1—H1	115 (2)	C7—C6—C5	119.6 (3)
C5—N2—C9	122.4 (2)	C7—C6—H6	120.2
C5—N2—H2	118 (2)	C5—C6—H6	120.2
C9—N2—H2	120 (2)	C6—C7—C8	121.0 (3)
C2—C1—C3^{i}	120.5 (3)	C6—C7—H7	119.5
C2—C1—H1A	119.7	C8—C7—H7	119.5
C3^{i}—C1—H1A	119.7	C9—C8—C7	118.4 (3)
C1—C2—C3	120.9 (3)	C9—C8—H8	120.8

C1—C2—H2A	119.6	C7—C8—H8	120.8
C3—C2—H2A	119.6	C8—C9—N2	121.2 (3)
C2—C3—C1^{i}	118.6 (3)	C8—C9—H9	119.4
C2—C3—C4	121.7 (3)	N2—C9—H9	119.4
C3^{i}—C1—C2—C3	0.3 (5)	C9—N2—C5—N1	179.5 (3)
C1—C2—C3—C1^{i}	−0.3 (4)	C9—N2—C5—C6	0.2 (4)
C1—C2—C3—C4	179.0 (2)	N1—C5—C6—C7	−179.0 (3)
C5—N1—C4—C3	80.0 (3)	N2—C5—C6—C7	0.3 (4)
C2—C3—C4—N1	−115.8 (3)	C5—C6—C7—C8	−0.5 (4)
C1^{i}—C3—C4—N1	63.5 (3)	C6—C7—C8—C9	0.2 (5)
C4—N1—C5—N2	8.5 (4)	C7—C8—C9—N2	0.3 (5)
C4—N1—C5—C6	−172.2 (3)	C5—N2—C9—C8	−0.5 (4)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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N1—H1···O4^{iv}	0.88 (1)	2.03 (1)	2.903 (3)	170 (3)

Symmetry codes: (ii) −*x*+1, −*y*+2, −*z*+2; (iii) −*x*, −*y*+2, −*z*+2; (iv) *x*, *y*−1, *z*.